IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In the matter of an application for a German Patent

in the name of Merck Patent GmbH, Darmstadt, Germany,

filed under No. 102 55 311.4

on 27 November 2002

and in the matter of an application for a United States Patent.

I, Dr. Ashwood Stephen DRANE, B.Sc., Ph.D., BDÜ, translator to SD Translations Ltd. of Beechwood, Chivery, Tring, Hertfordshire, HP23 6LD, England, do solemnly and sincerely declare:

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- 2. That I am well acquainted with the German and English languages and am a competent translator thereof.
- 3. That the following is to the best of my knowledge and belief a true and correct translation of the above-referenced patent application and the Official Certificate attached thereto

Dated this 16th day of April 2007

Dr. Ashwood Stephen Drane

FEDERAL REPUBLIC OF GERMANY



Priority certificate regarding the filing of a patent application

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Liquid-crystalline compounds

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The attached pages are a correct and accurate reproduction of the original documents of this patent application.

Seal

Munich, 24 June 2003

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Liquid-crystalline compounds

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Liquid-crystalline compounds

The present invention relates to liquid-crystalline compounds and to a liquid-crystalline medium, to the use thereof for electro-optical purposes, and to displays containing this medium.

Liquid crystals are used principally as dielectrics in display devices, since the optical properties of such substances can be modified by an applied voltage. Electro-optical devices based on liquid crystals are extremely well known to the person skilled in the art and can be based on various effects. Examples of such devices are cells having dynamic scattering, DAP (deformation of aligned phases) cells, guest/host cells, TN cells having a twisted nematic structure, STN (supertwisted nematic) cells, SBE (super-birefringence effect) cells and OMI (optical mode interference) cells. The commonest display devices are based on the Schadt-Helfrich effect and have a twisted nematic structure.

The liquid-crystal materials must have good chemical and thermal stability and good stability to electric fields and electromagnetic radiation. Furthermore, the liquid-crystal materials should have low viscosity and produce short addressing times, low threshold voltages and high contrast in the cells.

They should furthermore have a suitable mesophase, for example a nematic or cholesteric mesophase for the above-mentioned cells, at the usual operating temperatures, i.e. in the broadest possible range above and below room temperature. Since liquid crystals are generally used as mixtures of a plurality of components, it is important that the components are readily miscible with one another. Further properties, such as the electrical conductivity, the dielectric anisotropy and the optical anisotropy, have to satisfy various requirements depending on the cell type and area of application. For example, materials for cells having a twisted nematic structure should have positive dielectric anisotropy and low electrical conductivity.

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For example, for matrix liquid-crystal displays with integrated non-linear elements for switching individual pixels (MLC displays), media having large positive dielectric anisotropy, broad nematic phases, relatively low birefringence, very high specific resistance, good UV and temperature stability and low vapour pressure are desired.

Matrix liquid-crystal displays of this type are known. Non-linear elements which can be used for individual switching of the individual pixels are, for example, active elements (i.e. transistors). The term "active matrix" is then used, where a distinction can be made between two types:

- MOS (metal oxide semiconductor) or other diodes on a silicon wafer as substrate.
- 15 2. Thin-film transistors (TFTs) on a glass plate as substrate.

The use of single-crystal silicon as substrate material restricts the display size, since even modular assembly of various part-displays results in problems at the joins.

In the case of the more promising type 2, which is preferred, the electrooptical effect used is usually the TN effect. A distinction is made between two technologies: TFTs comprising compound semiconductors, such as, for example, CdSe, or TFTs based on polycrystalline or amorphous silicon.

Intensive work is being carried out world-wide on the latter technology.

The TFT matrix is applied to the inside of one glass plate of the display, while the other glass plate carries the transparent counterelectrode on its inside. Compared with the size of the pixel electrode, the TFT is very small and has virtually no adverse effect on the image. This technology can also be extended to fully colour-capable displays, in which a mosaic of red, green and blue filters is arranged in such a way that a filter element is opposite each switchable pixel.

The TFT displays usually operate as TN cells with crossed polarisers in transmission and are back-lit.

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The term MLC displays here encompasses any matrix display with integrated non-linear elements, i.e., besides the active matrix, also displays with passive elements, such as varistors or diodes (MIM = metal-insulator-metal).

MLC displays of this type are particularly suitable for TV applications (for example pocket television sets) or for high-information displays for computer applications (laptops) and in automobile or aircraft construction. Besides problems regarding the angle dependence of the contrast and the response times, difficulties also arise in MLC displays due to insufficiently high specific resistance of the liquid-crystal mixtures [TOGASHI, S., SEKI-GUCHI, K., TANABE, H., YAMAMOTO, E., SORIMACHI, K., TAJIMA, E., WATANABE, H., SHIMIZU, H., Proc. Eurodisplay 84, Sept. 1984: A 210-288 Matrix LCD Controlled by Double Stage Diode Rings, p. 141 ff, Paris; STROMER, M., Proc. Eurodisplay 84, Sept. 1984: Design of Thin Film Transistors for Matrix Addressing of Television Liquid Crystal Displays, p. 145 ff, Paris]. With decreasing resistance, the contrast of an MLC display deteriorates, and the problem of after-image elimination may occur. Since the specific resistance of the liquid-crystal mixture generally drops over the life of an MLC display owing to interaction with the interior surfaces of the display, a high (initial) resistance is very important in order to obtain acceptable service lives. In particular in the case of low-volt mixtures, it was hitherto impossible to achieve very high specific resistance values. It is furthermore important that the specific resistance exhibits the smallest possible increase with increasing temperature and after heating and/or UV exposure. The low-temperature properties of the mixtures from the prior art are also particularly disadvantageous. It is demanded that no crystallisation and/or smectic phases occur, even at low temperatures, and the temperature dependence of the viscosity is as low as possible. The MLC displays from the prior art thus do not meet today's requirements.

There thus continues to be a great demand for MLC displays having very high specific resistance at the same time as a large working-temperature range, short response times even at low temperatures and low threshold

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voltage which do not have these disadvantages, or only do so to a reduced extent.

In TN (Schadt-Helfrich) cells, media are desired which facilitate the following advantages in the cells:

- extended nematic phase range (in particular down to low temperatures)
- the ability to switch at extremely low temperatures (outdoor use, auto mobile, avionics)
 - increased resistance to UV radiation (longer service life).

The media available from the prior art do not allow these advantages to be achieved while simultaneously retaining the other parameters.

In the case of supertwisted (STN) cells, media are desired which enable greater multiplexability and/or lower threshold voltages and/or broader nematic phase ranges (in particular at low temperatures). To this end, a further widening of the available parameter latitude (clearing point, smectic-nematic transition or melting point, viscosity, dielectric parameters, elastic parameters) is urgently desired.

The invention has the object of providing media, in particular for MLC, IPS, TN or STN displays of this type, which do not have the above-mentioned disadvantages or only do so to a reduced extent, and preferably simultaneously have very high specific resistance values and low threshold voltages. This object requires liquid-crystalline compounds which have a high clearing point and low rotational viscosity.

It has now been found that this object can be achieved if the liquid-crystalline compounds according to the invention are used.

The invention thus relates to liquid-crystalline compounds of the formula I

$$R^{1}-(A^{1}-Z^{1})_{a}$$
 $-(Z^{2}-A^{2})_{b}$ $-CF_{2}O-(A^{3}-Z^{3})_{c}$ $-A^{4}-R^{2}$

5 in which

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R¹ and R²

viscosity.

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each, independently of one another, denote H, a halogenated or unsubstituted alkyl or alkoxy radical having 1 to 15 C atoms, where, in addition, one or more CH₂ groups in these radicals may each, independently of one another, be replaced by -C≡C-, -CH=CH-, -O-, -CO-O- or -O-CO- in such a way that O atoms are not linked directly to one another,

- 2¹, Z^2 and Z^3 each, independently of one another, denote -CO-O-, -O-CO-, -CF₂O-, -OCF₂-, -CH₂O-, -OCH₂-, -CH₂CH₂-, -(CH₂)₄-, -C₂F₄-, -CH₂CF₂-, -CF₂CH₂-, -CF=CF-, -CH=CH-, -C=C- or a single bond, and
- 20 a, b and c each, independently of one another, denote 0, 1 or 2, where $a + b + c \le 2$.

The invention furthermore relates to the use of the compounds of the formula I in liquid-crystalline media.

The compounds of the formula I have a broad range of applications.

Depending on the choice of substituents, these compounds can serve as base materials of which liquid-crystalline media are predominantly composed; however, it is also possible to add compounds of the formula I to liquid-crystalline base materials from other classes of compound in order, for example, to modify the dielectric and/or optical anisotropy of a dielectric of this type and/or in order to optimise its threshold voltage and/or its

In the pure state, the compounds of the formula I are colourless and form liquid-crystalline mesophases in a temperature range which is favourably

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located for electro-optical use. In particular, the compounds according to the invention are distinguished by their broad nematic phase range. In liquid-crystalline mixtures, the substances according to the invention suppress the smectic phases and result in a significant improvement in the low-temperature storage stability. They are stable chemically, thermally and to light.

The invention relates, in particular, to the compounds of the formula I in which R¹ is alkyl or alkenyl, and R² is F or OCF₃.

Particular preference is given to compounds of the formula I in which a = 0, furthermore a = 1. Z^1 , Z^2 and/or Z^3 is preferably a single bond, furthermore -CF₂O-, -OCF₂-, -C₂F₄-, -CH₂O-, -OCH₂- or -COO-.

15 Particular preference is given to compounds of the formulae IA

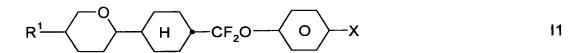
$$R^{1}$$
 H $CF_{2}O$ O IA

in which

a and b each denote 0, 1 or 2 and a + b = 1 or 2. Preferably, a = 1 and b = 0 or a = 0 and b = 1. Preferably, $L^1 = F$ and $L^2 = H$ or fluorine, in particular $L^1 = L^2 =$ fluorine.

 R^1 and X have the meanings indicated in Claim 1. X preferably denotes F or OCF₃, R^1 preferably denotes straight-chain alkyl or alkenyl. L^1 and L^2 each, independently of one another, denote H or F. Particular preference is given to compounds in which $X = L^1 = L^2 =$ fluorine, furthermore $X = OCF_3$ and $L^1 = L^2 = F$.

Particularly preferred compounds of the formula I are the compounds of the formulae I1 to I27



 $R^{1} \longrightarrow \begin{array}{c} O \\ H \end{array} \longrightarrow \begin{array}{c} F \\ CF_{2}O \longrightarrow \begin{array}{c} F \\ \end{array}$

15 $R^{1} \longrightarrow CH_{2}CH_{2} \longrightarrow H \longrightarrow CF_{2}O \longrightarrow X$ 14

 $R^{1} \longrightarrow CH_{2}CH_{2} \longrightarrow H \longrightarrow CF_{2}O \longrightarrow X$ I5

 R^1 CH_2CH_2 H CF_2O O X G

 $R^{1} \longrightarrow CF_{2}O \longrightarrow O \longrightarrow X$

$$R^1$$
 O H CF_2O O F X $I8$

$$R^1$$
 O H CF_2O O X $I10$

$$R^1$$
 \longrightarrow O \longrightarrow O \longrightarrow O \longrightarrow X I11

$$R^1$$
 CF_2O O COO O X $I13$

$$R^{1} \longrightarrow \begin{array}{c} O \\ H \end{array} \longrightarrow \begin{array}{c} CF_{2}O \longrightarrow \begin{array}{c} (F) \\ COO \longrightarrow \end{array} \longrightarrow \begin{array}{c} F \\ O \longrightarrow \end{array} \longrightarrow \begin{array}{c} I_{14} \\ I_{14} \end{array}$$

$$R^1$$
 CF_2O O COO O F COO CO

$$R^1$$
 CF_2O CF_2O O X $I16$

$$R^{1} \longrightarrow CF_{2}O \longrightarrow CF_{2}O \longrightarrow F$$

$$(F) \qquad F$$

$$I18$$

$$R^1$$
 H CF_2O O X $I19$

$$R^1$$
 H CF_2O O X $I20$

$$R^1$$
 H
 CF_2O
 O
 F
 $I21$

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$$R^1 \longrightarrow CF_2O \longrightarrow X$$
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$$R^{1} \longrightarrow \begin{array}{c} O \\ H \end{array} \longrightarrow \begin{array}{c} F \\ O \\ \end{array} \longrightarrow \begin{array}{c} F \\ O \\ \end{array} \longrightarrow \begin{array}{c} A \\ \end{array}$$

$$R^{1} \longrightarrow CF_{2}O \longrightarrow X$$

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$$R^1 \longrightarrow O \longrightarrow O \longrightarrow CF_2O \longrightarrow X$$
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$$R^1$$
 O O CF_2O O X $I27$

The compounds of the formula I are prepared by methods known per se, as described in the literature (for example in the standard works, such as Houben-Weyl, Methoden der organischen Chemie [Methods of Organic Chemistry], Georg-Thieme-Verlag, Stuttgart), to be precise under reaction conditions which are known and suitable for the said reactions. Use can

also be made here of variants known per se, which are not mentioned here in greater detail.

The compounds of the formula I can be prepared, for example, as follows:

Scheme 1

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$$R^{1}-A^{1}-Z^{1} \longrightarrow O \longrightarrow Br \longrightarrow R^{1}-A^{1}-Z^{1} \longrightarrow O \longrightarrow OH$$
1. BuLi, THF; -78°C
2. B(OMe)₃
3. NaOH, 30% $H_{2}O_{2}$;
40°C

1. TfOH,
$$CH_2CI_2$$
;
 $-60^{\circ}C/RT/-78^{\circ}C$
2. XPhOH, NEt_3 ;
 CH_2CI_2 , $-78^{\circ}C$
3. NEt_3 . 3 HF

4. DBH

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Scheme 2

$$R^{1}-A^{1}-Z^{1}$$
O
 $CF_{2}Br_{2}$, $P(NMe_{2})_{3}$, $R^{1}-A^{1}-Z^{1}$
O
 $R^{1}-A^{1}-Z^{1}$
THF/dioxane; RT, $R^{1}-A^{1}-Z^{1}$

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$$\frac{\mathsf{Br}_2, \; \mathsf{CH}_2\mathsf{Cl}_2}{\mathsf{0}^{\circ}\mathsf{C}} \qquad \mathsf{R}^1\text{-}\mathsf{A}^1\text{-}\mathsf{Z}^1 \qquad \qquad \mathsf{Br}$$

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$$\frac{\text{XPhONa, THF}}{} \quad \text{R}^{1}\text{-A}^{1}\text{-Z}^{1} \qquad \qquad \bigcirc \text{CF}_{2}\text{O} \qquad \bigcirc \text{O} \qquad X$$

15 80°C, THF

$$R^1-A^1-Z^1$$
 O H CF_2O O X

Scheme 3

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$$R^1-A^1-Z^1$$
 O Br $\frac{}{1. \text{ BuLi, THF; -40°C}}$ $R^1-A^1-Z^1$ O COOH

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$$\begin{array}{c|c} \hline \text{HS}(\text{CH}_2)_3\text{SH, TfOH,} \\ \hline \hline \text{Toluene/i-octane; -H}_2\text{O} \\ \hline \end{array} \quad \text{R}^1\text{-A}^1\text{-Z}^1 \quad \begin{array}{c|c} \hline \text{O} \\ \hline \end{array} \quad \begin{array}{c} \text{S}^{\overset{+}{\smile}} \\ \text{S} \\ \hline \end{array} \quad \text{CF}_3\text{SO}_3$$

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3. DBH

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Scheme 4

The invention also relates to electro-optical displays (in particular STN or MLC displays having two plane-parallel outer plates, which, together with a frame, form a cell, integrated non-linear elements for switching individual pixels on the outer plates, and a nematic liquid-crystal mixture of positive dielectric anisotropy and high specific resistance which is located in the cell) which contain media of this type, and to the use of these media for electro-optical purposes.

The liquid-crystal mixtures according to the invention enable a significant widening of the available parameter latitude.

The achievable combinations of clearing point, viscosity at low temperature, thermal and UV stability and dielectric anisotropy are far superior to previous materials from the prior art.

The requirement for a high clearing point, a nematic phase at low temperature and a high Δε has hitherto only been satisfied to an inadequate extent. Although liquid-crystal mixtures such as, for example, MS 99295 (Merck KGaA, Darmstadt, Germany) have comparable clearing points and low-temperature stabilities, they have, however, relatively high Δn values and also higher threshold voltages of about ≥ 1.7 V.

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Other mixture systems have comparable viscosities and $\Delta\epsilon$ values, but only have clearing points in the region of 60°C.

The liquid-crystal mixtures according to the invention, while retaining the nematic phase down to -20°C and preferably down to -30°C, particularly preferably down to -40°C, enable clearing points above 80°, preferably above 90°, particularly preferably above 100°C, simultaneously dielectric anisotropy values $\Delta \varepsilon$ of \geq 4, preferably \geq 6, and a high value for the specific resistance to be achieved, enabling excellent STN and MLC displays to be obtained. In particular, the mixtures are characterised by low operating voltages. The TN thresholds are below 1.5 V, preferably below 1.3 V.

It goes without saying that, through a suitable choice of the components of the mixtures according to the invention, it is also possible for higher clearing points (for example above 110°) to be achieved at a higher threshold voltage or lower clearing points to be achieved at lower threshold voltage with retention of the other advantageous properties. At viscosities correspondingly increased only slightly, it is likewise possible to obtain mixtures having greater $\Delta \varepsilon$ and thus lower thresholds. The MLC displays according to the invention preferably operate at the first Gooch and Tarry transmission minimum [C.H. Gooch and H.A. Tarry, Electron. Lett. 10, 2-4, 1974; C.H. Gooch and H.A. Tarry, Appl. Phys., Vol. 8, 1575-1584, 1975], where, besides particularly favourable electro-optical properties, such as, for example, high steepness of the characteristic line and low angle dependence of the contrast (German Patent 30 22 818), a lower dielectric anisotropy is sufficient at the same threshold voltage as in an analogous display at the second minimum. This enables significantly higher specific resistance values to be achieved using the mixtures according to the invention at the first minimum than in the case of mixtures comprising cyano compounds. Through a suitable choice of the individual

components and their proportions by weight, the person skilled in the art is able to set the birefringence necessary for a pre-specified layer thickness of the MLC display using simple routine methods.

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The flow viscosity v_{20} at 20°C is preferably < 60 mm² · s⁻¹, particularly preferably < 50 mm² · s⁻¹. The nematic phase range is preferably at least 90°, in particular at least 100°. This range preferably extends at least from -30° to +80°. The rotational viscosity γ_1 at 20°C is preferably < 200 mPa·s, particularly preferably < 180 mPa·s, in particular < 160 mPa·s.

Measurements of the capacity holding ratio (HR) [S. Matsumoto et al., Liquid Crystals <u>5</u>, 1320 (1989); K. Niwa et al., Proc. SID Conference, San Francisco, June 1984, p. 304 (1984); G. Weber et al., Liquid Crystals <u>5</u>, 1381 (1989)] have shown that mixtures according to the invention comprising compounds of the formula I exhibit a significantly smaller decrease in the HR with increasing temperature than analogous mixtures comprising cyanophenylcyclohexanes of the formula R (H) (O) CN or esters of

the formula R O C-O O CN instead of the compounds of the formula I.

The UV stability of the mixtures according to the invention is also considerably better, i.e. they exhibit a significantly smaller decrease in the HR on exposure to UV.

The media according to the invention are preferably based on a plurality of (preferably two, three or more) compounds of the formula I, i.e. the proportion of these compounds is 5-95%, preferably 10-60% and particularly preferably in the range 15-40%.

The individual compounds of the formulae I to IX and their sub-formulae which can be used in the media according to the invention are either known or they can be prepared analogously to the known compounds.

Preferred embodiments are indicated below:

 The medium preferably comprises one, two or three homologous compounds of the formula I, where each homologue is present in the mixture in a maximum amount of 10%.

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Medium additionally comprises one or more compounds selected from the group consisting of the general formulae II to IX:

10 $R^0 \longrightarrow H \longrightarrow C_2H_4 \longrightarrow O \longrightarrow X^0$

 $R^{0} \qquad H \qquad Z^{0} \qquad \qquad V$

 $R^{0} \xrightarrow{H} C_{2}H_{4} \xrightarrow{O} X^{0}$

 R^0 H Z^0 O X^0 VII

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$$R^0 \longrightarrow H \longrightarrow O \longrightarrow X^0$$
 VIII

 $R^0 \longrightarrow O \longrightarrow H \longrightarrow O \longrightarrow X^0$ IX

in which the individual radicals have the following meanings:

Ro n-alkyl, oxaalkyl, fluoroalkyl, alkenyloxy or alkenyl, each having up to 9 C atoms,

F, Cl, halogenated alkyl, halogenated alkenyl, halogenated alkenyloxy or halogenated alkoxy having up to 7 C atoms,

20 Z^0 -CH=CH-, -C₂H₄-, -(CH₂)₄-, -C₂F₄-, -CH₂O-, -OCH₂-, -CF=CF-, -CF₂O-, -OCF₂- or -COO-,

 Y^1 , Y^2 , Y^3 and Y^4 each, independently of one another, H or F, and r 0 or 1.

The compound of the formula IV is preferably

$$R^0 \longrightarrow H \longrightarrow O \longrightarrow F$$

$$R^0$$
 H O O X^0

 $R^0 \longrightarrow H \longrightarrow O \longrightarrow K^0 \longrightarrow K^0$

10 $R^0 \longrightarrow H \longrightarrow O \longrightarrow COO \longrightarrow K$

15 $R^0 \longrightarrow H \longrightarrow O \longrightarrow F \longrightarrow F$

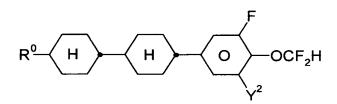
20 or

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 $R^0 \longrightarrow H \longrightarrow O \longrightarrow X^0$

- The medium preferably comprises one or more compounds of the formulae

 $R^{0} \longrightarrow H \longrightarrow O \longrightarrow OCF_{3}$



$$R^0$$
 H COO O F

$$R^0$$
 H O $-$ COO $-$ O F

$$R^0$$
 H O O F

$$R^0 \longrightarrow 0 \longrightarrow F$$

$$R^0$$
 H H O F

$$R^0$$
 H O F

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$$R^0$$
 H H O F

$$R^0$$
 H C_2F_4 H CF_2O O F

$$\mathsf{R}^0 \hspace{-0.1cm} \longleftarrow \hspace{-0.1cm} \hspace{-0.1cm} \mathsf{O} \hspace{-0.1cm} \longleftarrow \hspace{-0.1cm} \hspace{-0.1cm} \mathsf{COO} \hspace{-0.1cm} \longleftarrow \hspace{-0.1cm} \hspace{-0.1cm} \hspace{-0.1cm} \hspace{-0.1cm} \mathsf{O} \hspace{-0.1cm} \longrightarrow \hspace{-0.1cm} \hspace{-0.1cm} \mathsf{OCF}_3$$

15 and/or

$$R^0$$
 H O F

in which R⁰ and Y² have the meanings indicated above.

The medium preferably comprises one, two or three, furthermore four, homologues of the compounds selected from the group H1 to H19 (n = 1-7):

$$C_{n}H_{2n+1} - H - O - F + H1$$

$$C_nH_{2n+1}$$
 H O F $H2$

$$C_nH_{2n+1}$$
 H
 O
 F
 $H4$

$$C_nH_{2n+1}$$
 H
 C_2H_4
 H
 O
 F
 $H5$

$$C_nH_{2n+1}$$
 H C_2H_4 O F $H6$

$$C_nH_{2n+1}$$
 H O O F $H7$

$$C_nH_{2n+1}$$
 H O OCF_3 $H8$

$$C_nH_{2n+1}$$
 H CF_2O O F $H17$

$$C_nH_{2n+1}$$
 O O CF_2O O F $H19$

The medium additionally comprises one or more compounds selected from the group consisting of the general formulae X to XV:

$$R^0$$
 H H O X^0 X

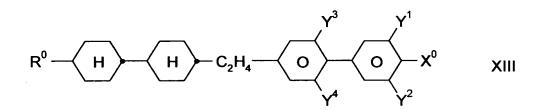
$$R^0$$
 H H CF_2O O XI

$$R^0$$
 H O XII

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 R^0 H C_2H_4 H O XIV

 R^0 H O O H XV

in which R^0 , X^0 , Y^1 , Y^2 , Y^3 and Y^4 each, independently of one another, have one of the meanings indicated in Claim 7. X^0 preferably denotes F, Cl, CF_3 , OCF_3 or $OCHF_2$. R^0 preferably denotes alkyl, oxaalkyl, fluoroalkyl, alkenyl or alkenyloxy.

- The proportion of compounds of the formulae I to IX together in the mixture as a whole is at least 50% by weight.
- The proportion of compounds of the formula I in the mixture as a whole is 5 to 50% by weight.
 - The proportion of compounds of the formulae II to IX in the mixture as a whole is 30 to 70% by weight.

- The medium comprises compounds of the formulae II, III, IV, V, VI, VII, VIII and/or IX.
- Ro denotes straight-chain alkyl or alkenyl having 2 to 7 C atoms.
 - The medium essentially consists of compounds of the formulae I to XV.
- The medium comprises further compounds, preferably selected from the following group consisting of the general formulae XVI to XX:

$$R^0 \longrightarrow O \longrightarrow O \longrightarrow X^0$$
 XVI

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$$R^0 - O - CH_2CH_2 - O - X^0$$
 XVII

XVIII

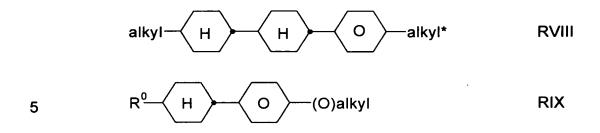
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$$R^0 - O - C_2H_4 - O - X^0$$

$$R^0 \longrightarrow O \longrightarrow F \longrightarrow XX$$

in which R⁰ and X⁰ have the meanings indicated above, and the 1,4phenylene rings may be substituted by CN, chlorine or fluorine. The 1,4phenylene rings are preferably mono- or polysubstituted by fluorine atoms.

The medium comprises further compounds, preferably selected from the following group consisting of the formulae RI to RIX



in which

10 R⁰ denotes n-alkyl, oxaalkyl, fluoroalkyl, alkenyloxy or alkenyl, each having up to 9 C atoms,

d denotes 0, 1 or 2,

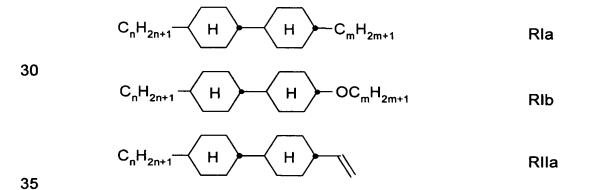
Y¹ denotes H or F,

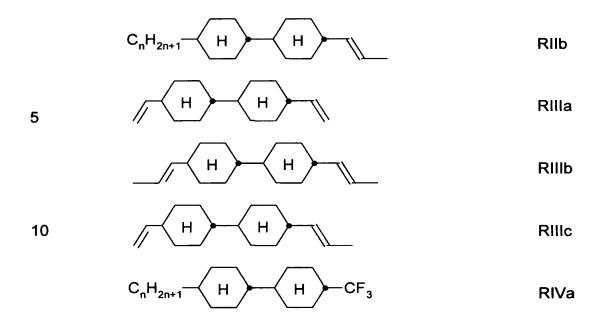
alkyl or

alkyl* each, independently of one another, denote a straight-chain or branched alkyl radical having 1-9 C atoms,

alkenyl or
alkenyl* each, independently of one another, denote a straight-chain
or branched alkenyl radical having up to 9 C atoms.

- The medium preferably comprises one or more compounds of the formulae





in which n and m each denote an integer from 1 to 9.

- The I: (II + III + IV + V + VI + VIII + IX) weight ratio is preferably 1: 10 to 10: 1.
- The medium essentially consists of compounds selected from the group consisting of the general formulae I to XV.
- the formula I mixed with conventional liquid-crystal materials, but in particular with one or more compounds of the formula II, III, IV, V, VI, VII, VIII or IX results in a considerable lowering of the threshold voltage and in low birefringence values, with broad nematic phases with low smectic-nematic transition temperatures being observed at the same time, improving the storage stability. The compounds of the formulae I to IX are colourless, stable and readily miscible with one another and with other liquid-crystal materials.
 - The term "alkyl" or "alkyl*" encompasses straight-chain and branched alkyl groups having 1-9 carbon atoms, in particular the straight-chain groups

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methyl, ethyl, propyl, butyl, pentyl, hexyl and heptyl. Groups having 2-5 carbon atoms are generally preferred.

The term "alkenyl" or "alkenyl*" encompasses straight-chain and branched alkenyl groups having up to 9 carbon atoms, in particular the straight-chain groups. Particularly preferred alkenyl groups are C₂-C₇-1E-alkenyl, C₄-C₇-3E-alkenyl, C₅-C₇-4-alkenyl, C₆-C₇-5-alkenyl and C₇-6-alkenyl, in particular C₂-C₇-1E-alkenyl, C₄-C₇-3E-alkenyl and C₅-C₇-4-alkenyl. Examples of preferred alkenyl groups are vinyl, 1E-propenyl, 1E-butenyl, 1E-pentenyl, 1E-hexenyl, 3E-hexenyl, 3E-hexenyl, 3E-hexenyl, 3E-hexenyl, 4Z-hexenyl, 4Z-hexenyl, 4Z-hexenyl, 4Z-hexenyl, and the like. Groups having up to 5 carbon atoms are generally preferred.

The term "fluoroalkyl" preferably encompasses straight-chain groups having a terminal fluorine, i.e. fluoromethyl, 2-fluoroethyl, 3-fluoropropyl, 4-fluorobutyl, 5-fluoropentyl, 6-fluorohexyl and 7-fluoroheptyl. However, other positions of the fluorine are not excluded.

The term "oxaalkyl" preferably encompasses straight-chain radicals of the formula C_nH_{2n+1} -O-(CH₂)_m, in which n and m each, independently of one another, denote 1 to 6. Preferably, n = 1 and m is 1 to 6.

Through a suitable choice of the meanings of R⁰ and X⁰, the addressing times, the threshold voltage, the steepness of the transmission characteristic lines, etc., can be modified in the desired manner. For example, 1E-alkenyl radicals, 3E-alkenyl radicals, 2E-alkenyloxy radicals and the like generally result in shorter addressing times, improved nematic tendencies and a higher ratio of the elastic constants k₃₃ (bend) and k₁₁ (splay) compared with alkyl or alkoxy radicals. 4-alkenyl radicals, 3-alkenyl radicals and the like generally give lower threshold voltages and smaller values of k₃₃/k₁₁ compared with alkyl and alkoxy radicals.

A -CH₂CH₂- group in Z¹ and/or Z² generally results in higher values of k₃₃/k₁₁ compared with a single covalent bond. Higher values of k₃₃/k₁₁ facilitate, for example, flatter transmission characteristic lines in TN cells

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with a 90° twist (in order to achieve grey shades) and steeper transmission characteristic lines in STN, SBE and OMI cells (greater multiplexability), and vice versa.

The optimum mixing ratio of the compounds of the formulae I and II + III + IV + V + VI + VII + VIII + IX depends substantially on the desired properties, on the choice of the components of the formulae I, II, III, IV, V, VI, VII, VIII and/or IX, and on the choice of any other components that may be present. Suitable mixing ratios within the range given above can easily be determined from case to case.

The total amount of compounds of the formulae I to XV in the mixtures according to the invention is not crucial. The mixtures can therefore comprise one or more further components for the purposes of optimisation of various properties. However, the observed effect on the addressing times and the threshold voltage is generally greater, the higher the total concentration of compounds of the formulae I to XV.

In a particularly preferred embodiment, the media according to the invention comprise compounds of the formulae II to IX (preferably II and/or III) in which X⁰ denotes OCF₃, OCHF₂, F, OCH=CF₂, OCF=CF₂, OCF₂CHFCF₃ or OCF₂-CF₂H. A favourable synergistic effect with the compounds of the formula I results in particularly advantageous properties.

The construction of the MLC display according to the invention from polarisers, electrode base plates and surface-treated electrodes corresponds to the conventional construction for displays of this type. The term conventional construction is broadly drawn here and also encompasses all derivatives and modifications of the MLC display, in particular including matrix display elements based on poly-Si TFT or MIM.

A significant difference between the displays according to the invention and the hitherto conventional displays based on the twisted nematic cell consists, however, in the choice of the liquid-crystal parameters of the liquid-crystal layer.

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The liquid-crystal mixtures which can be used in accordance with the invention are prepared in a manner conventional per se. In general, the desired amount of the components used in lesser amount is dissolved in the components making up the principal constituent, advantageously at elevated temperature. It is also possible to mix solutions of the components in an organic solvent, for example in acetone, chloroform or methanol, and to remove the solvent again, for example by distillation, after thorough mixing.

- The dielectrics may also comprise further additives known to the person skilled in the art and described in the literature, such as, for example stabilisers and antioxidants. For example, 0-15% of pleochroic dyes or chiral dopants can be added.
- 15 C denotes a crystalline phase, S a smectic phase, S_C a smectic C phase, S_B a smectic B phase, N a nematic phase and I the isotropic phase.

 V_{10} denotes the voltage for 10% transmission (viewing angle perpendicular to the plate surface). t_{on} denotes the switch-on time and t_{off} the switch-off time at an operating voltage corresponding to 2 times the value of V_{10} . Δn denotes the optical anisotropy and n_o the refractive index. $\Delta \epsilon$ denotes the dielectric anisotropy ($\Delta \epsilon = \epsilon_{||} - \epsilon_{\perp}$, where $\epsilon_{||}$ denotes the dielectric constant parallel to the longitudinal molecular axes and ϵ_{\perp} the dielectric constant perpendicular thereto). The electro-optical data were measured in a TN cell at the 1st minimum (i.e. at a d \cdot Δn value of 0.5) at 20°C, unless expressly stated otherwise. The optical data were measured at 20°C, unless expressly stated otherwise.

In the present application and in the examples below, the structures of the liquid-crystal compounds are indicated by means of acronyms, the transformation into chemical formulae taking place in accordance with Tables A and B below. All radicals C_nH_{2n+1} and C_mH_{2m+1} are straight-chain alkyl radicals having n and m C atoms respectively; n and m each, independently of one another, denote 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14 or 15. The coding in Table B is self-evident. In Table A, only the acronym for the parent structure is indicated. In individual cases, the acronym for the

parent structure is followed, separated by a dash, by a code for the substituents R^1 , R^2 , L^1 and L^2 :

5	Code for R ¹ , R ² , L ¹ , L ²	R ¹	R ²	L ¹	L ²
10	nm	C_nH_{2n+1}	C_mH_{2m+1}	Н	Н
	nOm	C_nH_{2n+1}	OC_mH_{2m+1}	Н	Н
	nO.m	OC_nH_{2n+1}	C_mH_{2m+1}	Н	Н
	n	C_nH_{2n+1}	CN	Н	Н
	nN.F	C_nH_{2n+1}	CN	Н	F
	nF	C_nH_{2n+1}	F	Н	Н
	nOF	OC_nH_{2n+1}	F	Н	Н
	nCl	C_nH_{2n+1}	CI	Н	Н
15	nF.F	C_nH_{2n+1}	F	Н	F
	nF.F.F	C_nH_{2n+1}	F	F	F
	nCF ₃	C_nH_{2n+1}	CF ₃	Н	Н
	nOCF ₃	C_nH_{2n+1}	OCF ₃	Н	Н
	nOCF ₂	C_nH_{2n+1}	OCHF ₂	Н	Н
20	nS	C_nH_{2n+1}	NCS	Н	Н
	rVsN	C _r H _{2r+1} -CH=CH-C _s H _{2s} -	CN	Н	Н
	rEsN	$C_rH_{2r+1}-O-C_2H_{2s}-$	CN	Н	Н
	nAm	C_nH_{2n+1}	$COOC_mH_{2m+1}$	Н	Н
	nOCCF ₂ .F.F	C_nH_{2n+1}	OCH₂CF₂H	F	F

Preferred mixture components are given in Tables A and B.

Table A:

30
$$R^{1} \longrightarrow O_{N}^{N} \longrightarrow O_{L^{2}}^{L^{1}}$$

$$R^{1} \longrightarrow O_{N}^{N} \longrightarrow O_{L^{2}}^{L^{1}}$$

$$PYP$$

$$PYRP$$

35

$$R^{1} \stackrel{}{\longleftarrow} H \stackrel{}{\longleftarrow} O \stackrel{}{\longrightarrow} C^{2} \qquad R^{1} \stackrel{}{\longleftarrow} H \stackrel{}{\longrightarrow} O \stackrel{}{\longrightarrow} H \stackrel{}{\longrightarrow} R^{2}$$

$$5 \qquad BCH \qquad CBC$$

$$R^{1} \stackrel{}{\longleftarrow} H \stackrel{}{\longleftarrow} H \stackrel{}{\longrightarrow} R^{2} \qquad R^{1} \stackrel{}{\longleftarrow} H \stackrel{}{\longleftarrow} O \stackrel{}{\longrightarrow} R^{2}$$

$$10 \qquad CCH \qquad CCP$$

$$R^{1} \stackrel{}{\longleftarrow} H \stackrel{}{\longleftarrow} C_{2}H_{4} \stackrel{}{\longleftarrow} O \stackrel{}{\longleftarrow} C \equiv C \stackrel{}{\longrightarrow} C^{2}$$

$$CEPTP$$

$$20 \qquad CEPTP$$

$$25 \qquad R^{1} \stackrel{}{\longleftarrow} H \stackrel{}{\longleftarrow} C_{2}H_{4} \stackrel{}{\longleftarrow} O \stackrel{}{\longrightarrow} C^{2}$$

$$ECCP$$

$$30 \qquad R^{1} \stackrel{}{\longleftarrow} H \stackrel{}{\longrightarrow} C_{2}H_{4} \stackrel{}{\longleftarrow} H \stackrel{}{\longrightarrow} O \stackrel{}{\longrightarrow} R^{2}$$

$$CECP$$

- 35 -

CCQU

$$R^1$$
 O O R^2 R^2

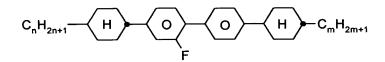
PGU

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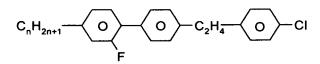
Table B:



CBC-nmF

$$C_nH_{2n+1}$$
 \longrightarrow O \longrightarrow OC_mH_{2m+1}

10 PCH-nOm



15 FET-nCI

$$C_nH_{2n+1}$$
 H H COO O OCF_3

CP-nOCF₃

$$C_nH_{2n+1}$$
 H OC_mH_{2m+1}

CCH-nOm

$$C_nH_{2n+1}$$
 H O X

BCH-n.Fm

$$C_nH_{2n+1}$$
 H C_2H_4 O C_mH_{2m+1}

Inm

$$C_nH_{2n+1}$$
 H O H C_mH_{2m+1}

CBC-nmF

$$C_nH_{2n+1}$$
 C_2H_4 O C_mH_{2m+1}

ECCP-nm

CCH-n1EM

$$C_nH_{2n+1} - O - O - C_mH_{2m+1}$$

T-nFm

CGU-n-F

CCP-nOCF₃.F

$$20 \qquad C_nH_{2n+1} \longrightarrow H \longrightarrow O \longrightarrow F$$

CGG-n-F

$$C_nH_{2n+1}$$
 H H O O OCF₂H

CCP-nOCF₂.F(.F)

$$c_nH_{2n+1}$$

CCP-nF.F.F

35

$$C_nH_{2n+1}$$
 H O F O $CH=CF_2$

5 CGU-n-OXF

10 CUZU-n-F

CGU-n-O1DT

15

20

$$C_nH_{2n+1}$$
 H COO F

CCZU-n-F

$$C_nH_{2n+1}$$
 H H H

25 CC-n-V1 CC-n-V

$$C_nH_{2n+1}$$
 H O OCF_3

30 CCP-nOCF₃

$$C_nH_{2n+1}$$
 \longrightarrow O \longrightarrow F

35 BCH-nF.F.F

$$C_nH_{2n+1}$$
 — C_2F_4 — CF_2O — CF_2O

5 CWCQU-n-F

$$C_nH_{2n+1}$$
 H CH_2O O C_mH_{2m+1}

CCOC-n-m

 $C_{n}H_{2n+1} \xrightarrow{\mathsf{H}} 0 \xrightarrow{\mathsf{F}} COO \xrightarrow{\mathsf{O}} F$

15 CGZU-n-F

$$C_nH_{2n+1}$$
 \longrightarrow COO \longrightarrow F

20 CUZP-n-F

25

30

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CCG-V-F

CGU-1V-F

$$C_nH_{2n+1}$$
 \longrightarrow COO \longrightarrow F

CGZP-n-F

$$C_nH_{2n+1}$$
 \longrightarrow COO \longrightarrow COO

UZP-n-N

$$C_nH_{2n+1}$$
 H O COO O OCF_3

CGZP-n-OT

5 C₀H₂₀₁₄ H O COO

CUZP-n-OT

10 C_nH_{2n+1} H CF_2O O

15 CCQU-n-F

$$C_nH_{2n+1}$$
 O O F C_nH_{2n+1} O O F

20 Dec-U-n-F

Nap-U-n-F

$$C_nH_{2n+1}$$
 H CF_2O O COO COO

25 CQGZP-n-F

$$C_nH_{2n+1}$$
 H H CF_2O O NCS

CCQP-n-S

$$C_nH_{2n+1}$$
 H O CF_2O F F

35 CPUQU-n-F

25

30

35

$$C_nH_{2n+1}$$
 H $(CH_2)_4$ C F

5 CCEEU-n-F $C_nH_{2n+1} - H - (CH_2)_4 - H - O - F$

15 CCQU-V-F

H - CF₂O - O F

CCQU-1V-F
$$CI \longrightarrow O \longrightarrow CF_2O \longrightarrow F$$

PUQU-CI-F
$$C_{n}H_{2n+1} \longrightarrow H \longrightarrow O \longrightarrow CF_{2}O \longrightarrow F$$

CGUQU-n-F
$$C_{n}H_{2n+1} \longrightarrow O \longrightarrow O \longrightarrow F$$

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PGU-n-F

$$Br \longrightarrow O \longrightarrow CF_2O \longrightarrow O \longrightarrow F$$

PQU-Br-F

$$F \longrightarrow O \longrightarrow CF_2O \longrightarrow F$$

PUQU-F-F

IS-9003

ACQU-n-F

$$C_nH_{2n+1}$$
 O O CF_2O O F

APUQU-n-F

30

Table C:

Table C shows possible dopants which are generally added to the mixtures according to the invention.

5

C 15

10

$$C_2H_5$$
-CH- CH_2
O
O
O
CN
 CH_3

CB 15

15

CM 21

20

25

R/S-811

$$C_3H_7$$
 H O CH_2 - $CH-C_2H_8$ CH_3

30

CM 44

35

CM 45

5 CM 47

CN

$$C_3H_7$$

H

O

F

CH

O

CH

O

F

CH

O

CH

O

A

O

F

CH

O

A

O

CH

O

A

O

CH

O

R/S-2011

$$C_5H_{11}$$
 O O C_6H_{13} O C_6H_{13}

R/S-4011

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Table D

Stabilisers which can be added, for example, to the mixtures according to the invention are mentioned below.

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The following examples are intended to explain the invention without restricting it. Above and below, percentages are per cent by weight. All temperatures are given in degrees Celsius. m.p. denotes melting point, cl.p. clearing point. Furthermore, C = crystalline state, N = nematic phase, S = smectic phase and I = isotropic phase. The data between these symbols represent the transition temperatures. Δn denotes optical anisotropy (589 nm, 20°C), $\Delta \epsilon$ the dielectric anisotropy (1 kHz, 20°C). The flow viscosity ν_{20} (mm²/sec) was determined at 20°C. The rotational viscosity γ_1 (mPa·s) was likewise determined at 20°C.

20

"Conventional work-up" means: water is added if necessary, the mixture is extracted with dichloromethane, diethyl ether, methyl tert-butyl ether or toluene, the phases are separated, the organic phase is dried and evaporated, and the product is purified by distillation under reduced pressure or crystallisation and/or chromatography. The following abbreviations are used:

25

	n-BuLi	1.6 molar solution of n-butyllithium in n-hexane
	DMAP	4-(dimethylamino)pyridine
30	THF	tetrahydrofuran
	DCC	N,N'-dicyclohexylcarbodiimide
	LDA	lithium dimethylamide

Example 1

$$_{5}$$
 $H_{7}C_{3}$ O H $CF_{2}O$ O F

Step 1.1

$$H_7C_3 \xrightarrow{CHO} H_7C_3 \xrightarrow{O} D$$

$$\underline{\underline{A}} \qquad \underline{\underline{B}}$$

15 B is prepared analogously to Lit. a) R. Baker, A. L. Boyes, C. J. Swain, J. Chem. Soc. Perkin Trans. 1, 1990, 1415-1421; b) H. Hagiwara, T. Okabe, H. Ono, V. P. Kamat, T. Hoshi, T. Suzuku, M. Ando, . Chem. Soc. Perkin Trans. 1, 2002, 895-900.

20 **Step 1.2**

30

35

$$H_7C_3$$
 O Br

25

207 mmol of BuLi (15% in hexane) are added dropwise at -50°C to a solution of 207 mmol of 1,4-dibromobenzene in 250 ml of diethyl ether. A solution of 170 mmol of **B** in 50 ml of diethyl ether is then added dropwise at the same temperature, and the mixture is stirred for a further 30 minutes, allowed to come to 0°C and subjected to conventional aqueous work-up. The crude product (51 g) is dissolved in 400 m l of CH₂Cl₂, and 400 mmol of triethylsilane are added at -75°C. 400 mmol of boron trifluoride etherate are added dropwise, during which the temperature must not rise above -70°C. The mixture is then allowed to come to -10°C, is hydrolysed using sat. NaHCO₃ solution and subjected to conventional aqueous work-up.

The crude product comprises the trans/cis isomers in a ratio of 9:1. The product is recrystallised from pentane at -20°C.

Step 1.3

5

$$H_7C_3$$
 O $B(OH)_2$

10

15

73 mmol of $\underline{\mathbf{C}}$ are dissolved in 200 ml of THF and cooled to -70°C. Firstly 73 mmol of BuLi (15% in hexane) followed by 73 mmol of trimethyl borate in 50 ml of THF are added dropwise. The mixture is allowed to come to -20°C, adjusted to pH = 2 by addition of 2N HCl and subjected to aqueous work-up. The crude product is digested with hot heptane and crystallised at 0°C.

Step 1.4

20

$$H_7C_3$$
 O O \bullet

25

A mixture of 60 mmol of $\underline{\mathbf{D}}$, 300 ml of toluene, 120 mmol of NaOH, 50 ml of water and 30 ml of 30% H_2O_2 is stirred at 45°C for 2 hours. The mixture is adjusted to pH = 2 using 10% HCl and subjected to aqueous work-up. The crude product is recrystallised from heptane.

<u>Step 1.5</u>

$$H_7C_3$$

35

22 mmol of <u>E</u> are hydrogenated at 5 bar and 130°C for 27.5 hours in 100 ml of xylene in the presence of 1.5 g of water-moist 5% Pd/C catalyst. Conventional work-up gives a colourless oil.

5 Step 1.6

10 <u>G</u>

17 mmol of BuLi (15% in hexane) are added at -70°C to a solution of 17 mmol of 2-trimethylsilyl-1,3-dithiane in 75 ml of THF. The mixture is allowed to come to 0°C over the course of 4 hours, then re-cooled to -70°C, 17 mmol of <u>F</u> in 25 ml of THF are added dropwise, and the mixture is allowed to come to room temperature, stirred for a further 18 hours and subjected to conventional aqueous work-up. The crude product is crystallised from heptane, giving colourless crystals.

20 Step 1.7

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$$H_7C_3$$
 O H CF_2O O F

H

6.27 mmol of trifluoromethanesulfonic acid are added dropwise at -20°C to a solution of 6.12 mmol of $\underline{\mathbf{G}}$ in 50 ml of $\mathrm{CH_2Cl_2}$. The mixture is allowed to come to room temperature for 30 minutes and then cooled to -70°C. Firstly a solution of 9.1 mmol of 3,4,4-trifluorophenol and 10.1 mmol of triethylamine in 20 l of $\mathrm{CH_2Cl_2}$ and 5 minutes later 31 mmol of triethylamine tris-(hydrofluoride) are then added. After a further 5 minutes, a suspension of 31.5 mmol of DBH (1,3-dibromo-5,5-dimethylhydanthoin) is added in small portions, and the mixture is stirred at -70°C for a further 1 hour. The reac-

tion mixture is allowed to come to -10°C and is poured into 400 ml of ice-cold NaOH. The mixture is subjected to conventional aqueous work-up, and the crude product is purified by chromatography on silica gel (heptane/toluene 3:2) and crystallisation from pentane at -70°C, giving colourless crystals: C 34 N 58.1 I.

The following compounds of the formula

10
$$R \longrightarrow H \longrightarrow CF_2O \longrightarrow C$$

are prepared analogously:

	R	X	L ¹	L ²	
	Н	F	Н	Н	
	CH₃	F	Н	Н	
20	C₂H₅	F	Н	Н	
	n-C₄H ₉	F	Н	Н	
	n-C ₅ H ₁₁	F	Н	Н	
	$n-C_6H_{13}$	F	Н	Н	
	Н	F	F	Н	
25	CH₃	F	F	Н	
	C_2H_5	F	F	Н	
	n-C ₃ H ₇	F	F	Н	
	n-C₄H ₉	F	F	Н	
	n-C₅H₁₁	F	F	Н	
30	n-C ₆ H ₁₃	F	F	Н	
	Н	F	F	F	
	CH₃	F	F	F	
	C ₂ H ₅	F	F	F	
	$n-C_3H_7$	F	F	F	
35	n-C₄H ₉	F	F	F	
	n-C₅H ₁₁	F	F	F	

	R	X	L ¹	L ²
	n-C ₆ H ₁₃	F	F	F
5	Н	CI	Н	Н
	CH₃	CI	Н	Н
	C ₂ H ₅	CI	Н	Н
	n-C ₃ H ₇	CI	Н	Н
	n-C₄H ₉	CI	Н	Н
	n-C ₅ H ₁₁	CI	Н	Н
	n-C ₆ H ₁₃	CI	Н	Н
10	Н	CI	F	Н
	CH₃	CI	F	Н
	C₂H₅	CI	F	Н
	n-C₃H ₇	CI	F	Н
	n-C₄H ₉	CI	F	Н
15	n-C₅H₁₁	CI	F	Н
	n-C ₆ H ₁₃	CI	F	Н
	Н	CI	F	F
	CH₃	CI	F	F
	C₂H₅	CI	F	F
20	n-C ₃ H ₇	CI	F	F
	n-C₄H ₉	CI	F	F
	n-C₅H₁₁	CI	F	F
	n-C ₆ H ₁₃	CI	F	F
	Н	OCF ₃	Н	Н
25	CH₃	OCF ₃	Н	Н
	C ₂ H ₅	OCF ₃	Н	Н
	n-C ₃ H ₇	OCF ₃	Н	Н
	n-C₄H ₉	OCF ₃	Н	Н
	n-C₅H ₁₁	OCF ₃	Н	Н
30	n-C ₆ H ₁₃	OCF ₃	Н	Н
	Н	OCF ₃	F	Н
	CH₃	OCF ₃	F	Н
	C ₂ H ₅	OCF ₃	F	Н
	n-C ₃ H ₇	OCF ₃	F	Н
35	n-C₄H ₉	OCF ₃	F	Н
	n-C ₅ H ₁₁	OCF ₃	F	Н

	R	x	L ¹	L ²
	n-C ₆ H ₁₃	OCF ₃	F	Н
	Н	OCF ₃	F	F
	CH₃	OCF ₃	F	F
5	C₂H₅	OCF ₃	F	F
	n-C₃H ₇	OCF ₃	F	F
	n-C₄H ₉	OCF ₃	F	F
	n-C₅H ₁₁	OCF ₃	F	F
	n-C ₆ H ₁₃	OCF ₃	F	F
10	Н	OCHF ₂	Н	Н
	CH₃	OCHF ₂	Н	Н
	C₂H₅	OCHF ₂	Н	Н
	n-C ₃ H ₇	OCHF ₂	Н	Н
	n-C₄H ₉	OCHF ₂	Н	Н
15	n-C₅H ₁₁	OCHF ₂	Н	Н
	n-C ₆ H ₁₃	OCHF ₂	Н	Н
	Н	OCHF ₂	F	Н
	CH₃	OCHF ₂	F	Н
	C ₂ H ₅	OCHF ₂	F	Н
20	$n-C_3H_7$	OCHF ₂	F	Н
	n-C₄H ₉	OCHF ₂	F	Н
	n-C₅H₁₁	OCHF ₂	F	Н
	n-C ₆ H ₁₃	OCHF ₂	F	Н
_	Н	OCHF ₂	F	F
25	CH₃	OCHF ₂	F	F
	C₂H₅	OCHF ₂	F	F
	n-C ₃ H ₇	OCHF ₂	F	F
	n-C₄H ₉	OCHF ₂	F	F
	$n-C_5H_{11}$	OCHF ₂	F	F
30	n-C ₆ H ₁₃	OCHF ₂	F	F
	Н	OCHFCF ₃	Н	Н
	CH₃	OCHFCF ₃	Н	Н
	C₂H₅	OCHFCF ₃	Н	Н
	n-C ₃ H ₇	OCHFCF ₃	Н	Н
35	n-C₄H ₉	OCHFCF ₃	Н	Н
	n-C ₅ H ₁₁	OCHFCF ₃	Н	Н

	R	×	L ¹	L ²
	n-C ₆ H ₁₃	OCHFCF ₃	Н	Н
	Н	OCHFCF ₃	F	Н
	CH₃	OCHFCF ₃	F	Н
5	C₂H₅	OCHFCF ₃	F	Н
	n-C ₃ H ₇	OCHFCF ₃	F	Н
	n-C₄H ₉	OCHFCF₃	F	Н
	n-C₅H₁₁	OCHFCF ₃	F	Н
	n-C ₆ H ₁₃	OCHFCF ₃	F	Н
10	Н	OCHFCF ₃	F	F
	CH₃	OCHFCF ₃	F	F
	C ₂ H ₅	OCHFCF ₃	F	F
	n-C ₃ H ₇	OCHFCF ₃	F	F
	n-C₄H ₉	OCHFCF ₃	F	F
15	n-C₅H ₁₁	OCHFCF ₃	F	F
	n-C ₆ H ₁₃	OCHFCF ₃	F	F
	Н	OCHFCF ₃	Н	Н
	CH₃	OCHFCF ₃	Н	Н
	C ₂ H ₅	OCHFCF ₃	Н	Н
20	n-C₃H ₇	OCHFCF ₃	Н	Н
	n-C₄H ₉	OCHFCF ₃	Н	Н
	n-C ₅ H ₁₁	OCHFCF ₃	Н	Н
	n-C ₆ H ₁₃	OCHFCF ₃	Н	Н
	Н	OCHFCF₃	F	Н
25	CH₃	OCHFCF ₃	F	Н
	C₂H₅	OCHFCF ₃	F	Н
	n-C₃H ₇	OCHFCF ₃	F	Н
	n-C₄H ₉	OCHFCF ₃	F	Н
	n-C₅H₁₁	OCHFCF ₃	F	Н
30	n-C ₆ H ₁₃	OCHFCF ₃	F	Н
	Н	OCHFCF ₃	F	F
	CH₃	OCHFCF ₃	F	F
	C_2H_5	OCHFCF ₃	F	F
0.5	n-C ₃ H ₇	OCHFCF ₃	F	F
35	n-C₄H ₉	OCHFCF ₃	F	F
	n-C₅H₁₁	OCHFCF ₃	F	F

	R	X	L ¹	L ²
	n-C ₆ H ₁₃	OCHFCF ₃	F	F
	Н	OCF ₂ CHFCF ₃	Н	Н
	CH₃	OCF ₂ CHFCF ₃	Н	Н
5	C₂H₅	OCF ₂ CHFCF ₃	Н	Н
	n-C ₃ H ₇	OCF ₂ CHFCF ₃	Н	Н
	n-C₄H ₉	OCF ₂ CHFCF ₃	Н	Н
	n-C₅H₁₁	OCF ₂ CHFCF ₃	Н	Н
	n-C ₆ H ₁₃	OCF ₂ CHFCF ₃	Н	Н
10	н	OCF ₂ CHFCF ₃	F	Н
	CH₃	OCF ₂ CHFCF ₃	F	Н
	C_2H_5	OCF ₂ CHFCF ₃	F	Н
	n-C ₃ H ₇	OCF ₂ CHFCF ₃	F	Н
	n-C₄H ₉	OCF ₂ CHFCF ₃	F	Н
15	n-C ₅ H ₁₁	OCF ₂ CHFCF ₃	F	Н
	n-C ₆ H ₁₃	OCF ₂ CHFCF ₃	F	Н
	Н	OCF ₂ CHFCF ₃	F	F
	CH₃	OCF ₂ CHFCF ₃	F	F
	C ₂ H ₅	OCF ₂ CHFCF ₃	F	F
20	n-C ₃ H ₇	OCF ₂ CHFCF ₃	F	F
	n-C₄H ₉	OCF ₂ CHFCF ₃	F	F
	n-C ₅ H ₁₁	OCF ₂ CHFCF ₃	F	F
	n-C ₆ H ₁₃	OCF ₂ CHFCF ₃	F [.]	F
	Н	NCS	Н	Н
25	CH₃	NCS	H	Н
	C₂H₅	NCS	Н	Н
	n-C ₃ H ₇	NCS	Н	Н
	n-C₄H ₉	NCS	Н	Н
	n-C ₅ H ₁₁	NCS	Н	Н
30	$n-C_6H_{13}$	NCS	Н	Н
	Н	NCS	F	Н
	CH₃	NCS	F	Н
	C_2H_5	NCS	F	Н
	n-C ₃ H ₇	NCS	F	Н
35	n-C₄H ₉	NCS	F	Н
	n-C ₅ H ₁₁	NCS	F	Н

	R	X	L ¹	L ²
	n-C ₆ H ₁₃	NCS	F	Н
	Н	NCS	F	F
	CH₃	NCS	F	F
5	C₂H₅	NCS	F	F
	n-C ₃ H ₇	NCS	F	F
	n-C₄H ₉	NCS	F	F
	n-C₅H₁₁	NCS	F	F
	n-C ₆ H ₁₃	NCS	F	F
10	Н	C_2F_5	Н	Н
	CH ₃	C ₂ F ₅	Н	Н
	C_2H_5	C ₂ F ₅	Н	Н
	n-C₃H ₇	C ₂ F ₅	Н	Н
	n-C ₄ H ₉	C ₂ F ₅	Н	Н
15	n-C₅H ₁₁	C ₂ F ₅	Н	Н
	n-C ₆ H ₁₃	C_2F_5	Н	Н
	Н	C ₂ F ₅	F	Н
	CH ₃	C ₂ F ₅	F	Н
	C ₂ H ₅	C_2F_5	F	Н
20	n-C₃H ₇	C ₂ F ₅	F	Н
	n-C₄H ₉	C_2F_5	F	Н
	n-C₅H₁₁	C_2F_5	F	Н
	n-C ₆ H ₁₃	C_2F_5	F	H
	Н	C ₂ F ₅	F	F
25	CH₃	C_2F_5	F	F
	C₂H₅	C ₂ F ₅	F	F
	n-C₃H ₇	C ₂ F ₅	F	F
	n-C₄H ₉	C_2F_5	F	F
00	n-C₅H ₁₁	C_2F_5	F	F
30	n-C ₆ H ₁₃	C_2F_5	F	F
	Н	C ₃ H ₇	Н	Н
	CH₃	C ₃ H ₇	Н	Н
	C ₂ H ₅	C ₃ H ₇	Н	Н
0.5	n-C ₃ H ₇	C_3H_7	Н	Н
35	n-C₄H ₉	C ₃ H ₇	Н	Н
	n-C₅H₁₁	C ₃ H ₇	Н	Н

	R	x	L¹	L ²
	n-C ₆ H ₁₃	C ₃ H ₇	Н	Н
	Н	C_3H_7	F	Н
5	CH₃	C ₃ H ₇	F	Н
	C₂H₅	C ₃ H ₇	F	Н
	n-C₃H ₇	C ₃ H ₇	F	Н
	n-C₄H ₉	C_3H_7	F	Н
	n-C₅H₁₁	C_3H_7	F	Н
	n-C ₆ H ₁₃	C_3H_7	F	Н
10	Н	C ₃ H ₇	F	F
	CH₃	C ₃ H ₇	F	F
	C ₂ H ₅	C_3H_7	F	F
	n-C ₃ H ₇	C_3H_7	F	F
	n-C₄H ₉	C_3H_7	F	F
15	n-C ₅ H ₁₁	C_3H_7	F	F
	n-C ₆ H ₁₃	C ₃ H ₇	F	F
	Н	SF ₅	Н	Н
	CH₃	SF ₅	Н	Н
	C_2H_5	SF ₅	Н	Н
20	n-C ₃ H ₇	SF ₅	Н	Н
	n-C₄H ₉	SF ₅	Н	Н
	n-C ₅ H ₁₁	SF ₅	Н	Н
	n-C ₆ H ₁₃	SF ₅	Н	Н
	Н	SF ₅	F	Н
25	CH₃	SF ₅	F	Н
	C₂H₅	SF ₅	F	Н
	n-C ₃ H ₇	SF ₅	F	Н
	n-C₄H ₉	SF₅	F	Н
	n-C ₅ H ₁₁	SF₅	F	Н
30	n-C ₆ H ₁₃	SF ₅	F	Н
	Н	SF ₅	F	F
	CH₃	SF ₅	F	F
	C₂H₅	SF ₅	F	F
	n-C ₃ H ₇	SF ₅	F	F
35	n-C₄H ₉	SF ₅	F	F
	n-C ₅ H ₁₁	SF ₅	F	F

	R	Χ	L ¹	L ²
	n-C ₆ H ₁₃	SF ₅	F	F
	Н	CN	Н	Н
	CH₃	CN	Н	Н
5	C₂H₅	CN	Н	Н
	n-C ₃ H ₇	CN	Н	Н
	n-C₄H ₉	CN	Н	Н
	n-C ₅ H ₁₁	CN	Н	Н
	n-C ₆ H ₁₃	CN	Н	Н
10	Н	CN	F	Н
	CH₃	CN	F	Н
	C_2H_5	CN	F	Н
	n-C ₃ H ₇	CN	F	Н
	n-C₄H ₉	CN	F	Н
15	n-C ₅ H ₁₁	CN	F	Н
	n-C ₆ H ₁₃	CN	F	Н
	Н	CN	F	F
	CH ₃	CN	F	F
	C₂H₅	CN	F	F
20	n-C ₃ H ₇	CN	F	F
	n-C₄H ₉	CN	F	F
	n-C ₅ H ₁₁	CN	F	F
	n-C ₆ H ₁₃	CN	F	F

25 <u>Example 2</u>

<u>Step 2.1</u>

30
$$H_{5}C_{2} \longrightarrow O \longrightarrow B(OH)_{2} + Br \longrightarrow CF_{2}O \longrightarrow F$$
35
$$\underline{I}$$

A mixture of 50 mmol of <u>I</u>, 50 mmol of <u>J</u>, 2.5 mmol of Pd(PPh₃)₄, 300 ml of toluene and 300 ml of Na borate buffer (pH = 9) is stirred at 80°C for 18 hours. The mixture is poured into 500 ml of 0.1 N HCl, and the product is extracted with CH₂Cl₂, dried over Na₂SO₄ and evaporated to dryness in a rotary evaporator. The crude product is chromatographed over silica gel in n-heptane and subsequently recrystallised twice from n-heptane at -20°C. C 77 N 90.8 I; Δn = 0.1493; Δε = 27.3

The following compounds of the formula

$$20 \qquad R \longrightarrow \begin{array}{c} O \\ O \\ \end{array} \longrightarrow \begin{array}{c} CF_2O \longrightarrow \begin{array}{c} C \\ O \\ \end{array} \longrightarrow \begin{array}{c} C \\ \end{array} \longrightarrow$$

are prepared analogously:

23					
	R	X	L ¹	L^2	
	Н	F	Н	Н	
	CH ₃	F	Н	Н	
	C ₂ H ₅	F	Н	Н	
30	C ₃ H ₇	F	Н	Н	
	n-C₄H ₉	F	Н	Н	
	n-C₅H₁₁	F	Н	Н	
	n-C ₆ H ₁₃	F	Н	Н	
	Н	F	F	Н	
35	CH ₃	F	F	Н	
	C ₂ H ₅	F	F	Н	

	R	x	L ¹	L ²
	n-C ₃ H ₇	F	F	Н
	n-C₄H ₉	F	F	Н
5	n-C₅H ₁₁	F	F	Н
	n-C ₆ H ₁₃	F	F	Н
	Н	F	F	F
	CH ₃	F	F	F
	n-C₃H ₇	F	F	F
	n-C₄H ₉	F	F	F
10	n-C₅H ₁₁	F	F	F
	n-C ₆ H ₁₃	F	F	F
	Н	CI	Н	Н
	CH₃	CI	Н	Н
	C ₂ H ₅	CI	Н	Н
15	n-C₃H ₇	CI	Н	Н
	n-C₄H ₉	CI	Н	Н
	n-C₅H₁₁	CI	Н	Н
	n-C ₆ H ₁₃	CI	Н	Н
	Н	CI	F	Н
20	CH₃	CI	F	Н
	C_2H_5	CI	F	Н
	n-C₃H ₇	CI	F	Н
	n-C₄H ₉	CI	F	Н
	n-C₅H₁₁	CI	F	Н
25	n-C ₆ H ₁₃	CI	F	Н
	Н	CI	F	F
	CH₃	CI	F	F
	C₂H₅	CI	F	F
	n-C₃H ₇	CI	F	F
30	n-C₄H ₉	CI	F	F
	n-C₅H ₁₁	CI	F	F
	n-C ₆ H ₁₃	CI	F	F
	Н	OCF ₃	Н	Н
^-	CH ₃	OCF ₃	Н	Н
35	C₂H₅	OCF ₃	Н	Н
	n-C₃H ₇	OCF ₃	Н	Н

	R	X	L ¹	L ²
	n-C₄H ₉	OCF ₃	Н	Н
	n-C₅H₁₁	OCF ₃	Н	Н
	n-C ₆ H ₁₃	OCF ₃	Н	Н
5	Н	OCF ₃	F	Н
	CH ₃	OCF ₃	F	Н
	C_2H_5	OCF ₃	F	Н
	n-C ₃ H ₇	OCF ₃	F	Н
	n-C₄H ₉	OCF ₃	F	Н
10	n-C ₅ H ₁₁	OCF ₃	F	Н
	n-C ₆ H ₁₃	OCF ₃	F	Н
	Н	OCF ₃	F	F
	CH₃	OCF ₃	F	F
	C₂H₅	OCF ₃	F	F
15	n-C₃H ₇	OCF ₃	F	F
	n-C₄H ₉	OCF ₃	F	F
	n-C₅H ₁₁	OCF ₃	F	F
	n-C ₆ H ₁₃	OCF ₃	F	F
	Н	OCHF ₂	Н	Н
20	CH₃	OCHF ₂	Н	Н
	C ₂ H ₅	OCHF ₂	Н	H
	n-C ₃ H ₇	OCHF ₂	Н	Н
	n-C₄H ₉	OCHF ₂	Н	Н
	n-C ₅ H ₁₁	OCHF ₂	Н	H
25	n-C ₆ H ₁₃	OCHF ₂	Н	Н
	Н	OCHF ₂	F	Н
	CH₃	OCHF ₂	F	Н
	C ₂ H ₅	OCHF ₂	F	Н
	n-C ₃ H ₇	OCHF ₂	F	Н
30	n-C₄H ₉	OCHF ₂	F	Н
	n-C₅H ₁₁	OCHF ₂	F	Н
	n-C ₆ H ₁₃	OCHF ₂	F	Н
	Н	OCHF ₂	F	F
	CH₃	OCHF ₂	F	F
35	C_2H_5	OCHF ₂	F	F
	n-C ₃ H ₇	OCHF ₂	F	F

	R	X	L ¹	L ²	
	n-C₄H ₉	OCHF ₂	F	F	
	n-C₅H₁₁	OCHF ₂	F	F	
	n-C ₆ H ₁₃	OCHF ₂	F	F	
5	Н	OCHFCF ₃	Н	Н	
	CH₃	OCHFCF₃	Н	Н	
	C_2H_5	OCHFCF₃	Н	Н	
	n-C ₃ H ₇	OCHFCF₃	Н	Н	
	n-C₄H ₉	OCHFCF ₃	Н	Н	
10	n-C₅H₁₁	OCHFCF₃	Н	Н	
	$n-C_6H_{13}$	OCHFCF ₃	Н	Н	
	Н	OCHFCF ₃	F	Н	
	CH ₃	OCHFCF ₃	F	Н	
	C ₂ H ₅	OCHFCF ₃	F	Н	
15	$n-C_3H_7$	OCHFCF ₃	F	Н	
	n-C₄H ₉	OCHFCF₃	F	Н	
	n-C₅H₁₁	OCHFCF ₃	F	Н	
	n-C ₆ H ₁₃	OCHFCF ₃	F	Н	
	Н	OCHFCF ₃	F	F	
20	CH ₃	OCHFCF ₃	F	F	
	C ₂ H ₅	OCHFCF ₃	F	F	
	n-C₃H ₇	OCHFCF ₃	F	F	
	n-C₄H ₉	OCHFCF ₃	F	F	
	$n-C_5H_{11}$	OCHFCF₃	F	F	
25	n-C ₆ H ₁₃	OCHFCF ₃	F	F	
	Н	OCHFCF ₃	Н	Н	
	CH₃	OCHFCF ₃	Н	Н	
	C_2H_5	OCHFCF ₃	Н	Н	
	n-C ₃ H ₇	OCHFCF ₃	Н	Н	
30	n-C₄H ₉	OCHFCF ₃	Н	Н	
	n-C ₅ H ₁₁	OCHFCF₃	Н	Н	
	n-C ₆ H ₁₃	OCHFCF ₃	Н	Н	
	Н	OCHFCF ₃	F	Н	
a =	CH₃	OCHFCF ₃	F	Н	
35	C_2H_5	OCHFCF ₃	F	Н	
	$n-C_3H_7$	OCHFCF ₃	F	Н	

	R	x	L ¹	L ²
	n-C₄H ₉	OCHFCF ₃	F	Н
	n-C ₅ H ₁₁	OCHFCF ₃	F	Н
	n-C ₆ H ₁₃	OCHFCF ₃	F	Н
5	Н	OCHFCF ₃	F	F
	CH₃	OCHFCF ₃	F	F
	C₂H₅	OCHFCF ₃	F	F
	n-C ₃ H ₇	OCHFCF ₃	F	F
	n-C₄H ₉	OCHFCF ₃	F	F
10	n-C ₅ H ₁₁	OCHFCF ₃	F	F
	n-C ₆ H ₁₃	OCHFCF ₃	F	F
	Н	OCF ₂ CHFCF ₃	Н	Н
	CH ₃	OCF₂CHFCF₃	Н	Н
	C ₂ H ₅	OCF₂CHFCF₃	Н	Н
15	n-C₃H ₇	OCF ₂ CHFCF ₃	Н	Н
	n-C₄H ₉	OCF ₂ CHFCF ₃	Н	Н
	n-C₅H ₁₁	OCF ₂ CHFCF ₃	Н	Н
	n-C ₆ H ₁₃	OCF ₂ CHFCF ₃	Н	Н
	Н	OCF ₂ CHFCF ₃	F	Н
20	CH₃	OCF ₂ CHFCF ₃	F	Н
	C_2H_5	OCF ₂ CHFCF ₃	F	Н
	n-C ₃ H ₇	OCF ₂ CHFCF ₃	F	Н
	n-C₄H ₉	OCF ₂ CHFCF ₃	F	Н
_	n-C ₅ H ₁₁	OCF ₂ CHFCF ₃	F	Н
25	n-C ₆ H ₁₃	OCF ₂ CHFCF ₃	F	Н
	Н	OCF ₂ CHFCF ₃	F	F
	CH ₃	OCF ₂ CHFCF ₃	F	F
	C_2H_5	OCF ₂ CHFCF ₃	F	F
	n-C ₃ H ₇	OCF ₂ CHFCF ₃	F	F
30	n-C₄H ₉	OCF ₂ CHFCF ₃	F	F
	n-C₅H ₁₁	OCF ₂ CHFCF ₃	F	F
	n-C ₆ H ₁₃	OCF ₂ CHFCF ₃	F	F
	Н	NCS	Н	Н
	CH₃	NCS	Н	Н
35	C_2H_5	NCS	Н	Н
	n-C ₃ H ₇	NCS	Н	Н

	R	X	L^1	L^2	
	n-C₄H ₉	NCS	Н	Н	
	n-C ₅ H ₁₁	NCS	Н	Н	
	n-C ₆ H ₁₃	NCS	Н	Н	
5	Н	NCS	F	Н	
	СН₃	NCS	F	Н	
	C₂H₅	NCS	F	Н	
	n-C₃H ₇	NCS	F	Н	
40	n-C ₄ H ₉	NCS	F	Н	
10	n-C₅H₁₁	NCS	F	Н	
	n-C ₆ H ₁₃	NCS	F	Н	
	Н	NCS	F	F	
	СН₃	NCS	F	F	
	C₂H₅	NCS	F	F	
15	n-C₃H ₇	NCS	F	F	
	n-C₄H ₉	NCS	F	F	
	n-C₅H₁₁	NCS	F	F	
	n-C ₆ H ₁₃	NCS	F	F	
	Н	C_2F_5	Н	Н	
20	CH₃	C₂F₅	Н	Н	
	C ₂ H ₅	C_2F_5	Н	Н	
	n-C ₃ H ₇	C ₂ F ₅	Н	Н	
	n-C₄H ₉	C_2F_5	F F H H H H H F F	Н	
	n-C ₅ H ₁₁	C_2F_5	Н	Н	
25	n-C ₆ H ₁₃	C_2F_5	Н	Н	
	Н	C_2F_5	F	Н	
	CH₃	C₂F₅	F	Н	
	C ₂ H ₅	C_2F_5	F	Н	
30	n-C₃H ₇	C_2F_5	F	Н	
	n-C₄H ₉	C_2F_5	F	Н	
	n-C ₅ H ₁₁	C_2F_5	F	Н	
	n-C ₆ H ₁₃	C_2F_5	F	Н	
	Н	C_2F_5	F	F	
	CH₃	C_2F_5	F	F	
35	C₂H₅	C_2F_5	F	F	
	n-C ₃ H ₇	C_2F_5	F	F	

	R	X	L ¹	L ²
	n-C₄H ₉	C ₂ F ₅	F	F
	n-C₅H ₁₁	C_2F_5	F	F
_	n-C ₆ H ₁₃	C_2F_5	F	F
5	Η .	C ₃ H ₇	Н	Н
	CH ₃	C ₃ H ₇	Н	Н
	C ₂ H ₅	C ₃ H ₇	Н	Н
	n-C ₃ H ₇	C ₃ H ₇	Н	Н
	n-C₄H ₉	C ₃ H ₇	Н	Н
10	n-C₅H₁₁	C ₃ H ₇	Н	Н
	n-C ₆ H ₁₃	C ₃ H ₇	Н	Н
	Н	C_3H_7	F	Н
	CH₃	C ₃ H ₇	F F H H H H H H	Н
	C₂H₅	C ₃ H ₇ H H C ₃ H ₇ F C ₃ H ₇	Н	
15	n-C ₃ H ₇	C ₃ H ₇	F	Н
	n-C₄H ₉	C ₃ H ₇	F	Н
	n-C₅H ₁₁	C ₃ H ₇	F	Н
	n-C ₆ H ₁₃	C ₃ H ₇	F	Н
	Н	C ₃ H ₇	F	F
20	CH₃	C ₃ H ₇	F	F
	C₂H₅	C ₃ H ₇	F	F
	n-C ₃ H ₇	C ₃ H ₇	F	F
	n-C₄H ₉	C₃H ₇	F F F H H H H H H H F F F F F F F F F F	F
	n-C ₅ H ₁₁	C ₃ H ₇ H C ₃ H ₇ F S ₅ H SF ₅ H SF ₅ H SF ₅ F	F	
25	n-C ₆ H ₁₃	C ₃ H ₇	F	F
	Н	SF ₅	Н	Н
	CH ₃	SF ₅	Н	H
n-C n-C n-C n-C n-C 10 n-C	C₂H₅	SF₅	Н	Н
	n-C₃H ₇	SF ₅	Н	Н
30	n-C₄H ₉	SF ₅	Н	Н
	n-C₅H₁₁	SF ₅	Н	Н
	n-C ₆ H ₁₃	SF ₅	Н	Н
	Н	SF₅	F H H H H H H H F F F F F F F F F F F H H H H H H H H H F F F	Н
	CH ₃	SF ₅	F	Н
35	C ₂ H ₅	SF₅	F	Н
	n-C ₃ H ₇	SF ₅	F	Н

	R	X	L ¹	L ²
	n-C₄H ₉	SF ₅	F	Н
	n-C₅H ₁₁	SF ₅	F	Н
5	n-C ₆ H ₁₃	SF ₅	F	Н
	Н	SF ₅	F	F
	CH₃	SF ₅	F	F
	C₂H₅	SF ₅	F	F
	n-C ₃ H ₇	SF ₅	F	F
10	n-C₄H ₉	SF ₅	F	F
	n-C₅H ₁₁	SF ₅	F	F
	n-C ₆ H ₁₃	SF ₅	F	F
	Н	CN	Н	Н
15	CH₃	CN	Н	Н
	C ₂ H ₅	CN	Н	Н
15	n-C ₃ H ₇	CN	Н	Н
	n-C₄H ₉	CN	Н	Н
	n-C ₅ H ₁₁	CN	Н	Н
	n-C ₆ H ₁₃	CN	Н	Н
	Н	CN	F	Н
20	CH₃	CN	F	Н
	C ₂ H ₅	CN	F	Н
	n-C ₃ H ₇	CN	F	Н
	n-C₄H ₉	CN	F	Н
	n-C ₅ H ₁₁	CN	F	Н
25	n-C ₆ H ₁₃	CN	F	Н
	Н	CN	F	F
	CH₃	CN	F	F
	C₂H₅	CN	F	F
	n-C ₃ H ₇	CN	F	F
30	n-C₄H ₉	CN	F	F
	n-C₅H₁₁	CN	F	F
	n-C ₆ H ₁₃	CN	F	F

Example 3

Step 3.1

62.7 mmol of trifluoromethanesulfonic acid are added dropwise at -20°C to a solution of 61.2 mmol of <u>L</u> in 500 ml of CH₂Cl₂. The mixture is allowed to come to room temperature for 30 minutes and then cooled to -70°C. Firstly a solution of 91 mmol of 4-bromo-3-fluorophenol and 101 mmol of triethylamine in 200 ml of CH₂Cl₂ and 5 minutes later 310 mmol of triethylamine tris(hydrofluoride) are then added. After a further 5 minutes, a suspension of 315 mmol of 1,3-dibromo-5,5-dimethylhydanthoin is added in small portions, and the mixture is stirred at -70°C for a further 1 hour. The reaction mixture is allowed to come to -10°C and is poured into ice-cold NaOH. The mixture is subjected to conventional aqueous work-up, and the crude product is purified by chromatography on silica gel (heptane/MTB ether 4:1) and crystallisation from ethanol at -20°C.

20

25

15

25

Step 3.2

$$_{5}$$
 $C_{3}H_{7}$ O H $CF_{2}O$ O F

A mixture of 50 mmol of $\underline{\mathbf{M}}$, 50 mmol of 3,4,5-trifluorobenzeneboronic acid, 2.5 mmol of Pd(PPh₃)₄, 300 ml of toluene and 300 ml of Na borate buffer (pH = 9) is stirred at 80°C for 18 hours. The mixture is poured into 500 ml of 0.1 N HCl, and the product is extracted with CH₂Cl₂, dried over Na₂SO₄ and evaporated to dryness in a rotary evaporator. The crude product is chromatographed over silica gel in n-heptane and subsequently recrystal-lised from n-heptane at -20°C. C 61 N 191.8 I; Δ n = 0.1220; Δ ϵ = 19.1

The following compounds of the formula

$$20 \qquad R \longrightarrow \begin{array}{c} O \\ H \end{array} \longrightarrow \begin{array}{c} CF_2O \longrightarrow \begin{array}{c} C \\ O \end{array} \longrightarrow \begin{array}{c} C \\ C \end{array} \longrightarrow \begin{array}{c} C \end{array} \longrightarrow \begin{array}{c} C \\ C \end{array} \longrightarrow \begin{array}{c} C \end{array} \longrightarrow \begin{array}{c} C \\ C \end{array} \longrightarrow \begin{array}{c} C \end{array} \longrightarrow \begin{array}{c} C \end{array} \longrightarrow \begin{array}{c} C \\ C \end{array} \longrightarrow \begin{array}{c} C \end{array} \longrightarrow \begin{array}{c} C \\ C \end{array} \longrightarrow \begin{array}{c} C \end{array} \longrightarrow \begin{array}{c} C$$

are prepared analogously:

25					
	R	X	L ¹	L ²	
	Н	F	Н	Н	
	CH₃	F	Н	Н	
	C ₂ H ₅	F	Н	Н	
30	n-C₄H ₉	F	Н	Н	
	n-C₅H₁₁	F	Н	Н	
	$n-C_6H_{13}$	F	Н	Н	
	Н	F	F	Н	
	CH ₃	F	F	Н	
35	C_2H_5	F	F	Н	
	n-C ₃ H ₇	F	F	Н	

	R	X	L ¹	L ²	
	n-C ₄ H ₉	F	F	Н	
	n-C ₅ H ₁₁	F	F	Н	
	n-C ₆ H ₁₃	F	F	Н	
5	Н	F	F	F	
	CH₃	F	F	F	
	C₂H₅	F	F	F	
	n-C ₃ H ₇	F	F	F	
	n-C₄H ₉	F	F	F	
10	n-C₅H₁₁	F	F	F	
	n-C ₆ H ₁₃	F	F	F	
	Н	CI	Н	Н	
	CH₃	CI	Н	Н	
	C₂H₅	Cl	Н	Н	
15	$n-C_3H_7$	CI	Н	Н	
	n-C₄H ₉	CI	Н	Н	
	n-C₅H₁₁	CI	Н	Н	
	n-C ₆ H ₁₃	CI	Н	Н	
	Н	CI	F	Н	
20	CH ₃	Cl	F	Н	
	C ₂ H ₅	CI	F	Н	
	n-C₃H ₇	CI	F	н	
	n-C₄H ₉	CI	F	Н	
	$n-C_5H_{11}$	CI	F	Н	
25	n-C ₆ H ₁₃	CI	F	Н	
	Н	CI	F	F	
	CH₃	CI	F	F	
	C_2H_5	CI	F	F	
	n-C ₃ H ₇	Cl	F	F	
30	n-C₄H ₉	Cl	F	F	
	n-C₅H₁₁	CI	F	F	
	$n-C_6H_{13}$	CI	F	F	
	Н	OCF ₃	Н	Н	
0.5	CH₃	OCF ₃	Н	Н	
35	C ₂ H ₅	OCF ₃	Н	Н	
	$n-C_3H_7$	OCF ₃	Н	Н	

	R	×	L ¹	L ²
	n-C₄H ₉	OCF ₃	Н	Н
	n-C₅H₁₁	OCF ₃	Н	Н
	n-C ₆ H ₁₃	OCF ₃	Н	Н
5	Н	OCF ₃	F	Н
	CH₃	OCF ₃	F	Н
	C_2H_5	OCF ₃	F	Н
	n-C ₃ H ₇	OCF ₃	F	Н
	n-C₄H ₉	OCF ₃	F	Н
10	n-C₅H₁₁	OCF ₃	F	Н
	n-C ₆ H ₁₃	OCF ₃	F	Н
	Н	OCF ₃	F	F
	CH₃	OCF ₃	F	F
	C₂H₅	OCF ₃	F	F
15	n-C ₃ H ₇	OCF ₃	F	F
	n-C₄H ₉	OCF ₃	F	F
	n-C ₅ H ₁₁	OCF ₃	F	F
	n-C ₆ H ₁₃	OCF ₃	F	F
	Н	OCHF ₂	Н	Н
20	CH₃	OCHF ₂	Н	Н
	C ₂ H ₅	OCHF ₂	Н	Н
	n-C ₃ H ₇	OCHF ₂	Н	Н
	n-C₄H ₉	OCHF ₂	Н	Н
	n-C ₅ H ₁₁	OCHF ₂	Н	Н
25	n-C ₆ H ₁₃	OCHF ₂	Н	Н
	Н	OCHF ₂	F	Н
	CH₃	OCHF ₂	F	Н
	C₂H₅	OCHF ₂	F	Н
	n-C ₃ H ₇	OCHF ₂	F	Н
30	n-C₄H ₉	OCHF ₂	F	Н
	n-C ₅ H ₁₁	OCHF ₂	F	Н
	n-C ₆ H ₁₃	OCHF ₂	F	Н
	Н	OCHF ₂	F	F
	CH₃	OCHF ₂	F	F
35	C₂H₅	OCHF ₂	F	F
	$n-C_3H_7$	OCHF ₂	F	F

	R	x	L ¹	L ²
	n-C₄H ₉	OCHF ₂	F	F
	n-C₅H ₁₁	OCHF ₂	F	F
	n-C ₆ H ₁₃	OCHF ₂	F	F
5	Н	OCHFCF ₃	Н	Н
	CH₃	OCHFCF ₃	Н	Н
	C₂H₅	OCHFCF ₃	Н	Н
	n-C ₃ H ₇	OCHFCF ₃	Н	Н
	n-C₄H ₉	OCHFCF ₃	Н	Н
10	n-C ₅ H ₁₁	OCHFCF ₃	H ·	Н
	n-C ₆ H ₁₃	OCHFCF ₃	Н	Н
	Н	OCHFCF ₃	F	Н
	CH₃	OCHFCF ₃	F	Н
	C ₂ H ₅	OCHFCF ₃	F	Н
15	n-C ₃ H ₇	OCHFCF ₃	F	Н
	n-C₄H ₉	OCHFCF ₃	F	Н
	n-C₅H ₁₁	OCHFCF ₃	F	Н
	n-C ₆ H ₁₃	OCHFCF ₃	F	Н
	H	OCHFCF ₃	F	F
20	CH₃	OCHFCF ₃	F	F
	C_2H_5	OCHFCF ₃	F	F
	n-C ₃ H ₇	OCHFCF ₃	F	F
	n-C₄H ₉	OCHFCF ₃	F	F
	n-C ₅ H ₁₁	OCHFCF ₃	F	F
25	n-C ₆ H ₁₃	OCHFCF ₃	F	F
	Н	OCHFCF ₃	Н	Н
	CH₃	OCHFCF ₃	Н	Н
	C₂H₅	OCHFCF ₃	Н	Н
	n-C ₃ H ₇	OCHFCF ₃	Н	Н
30	n-C₄H ₉	OCHFCF ₃	Н	Н
	n-C ₅ H ₁₁	OCHFCF ₃	Н	Н
	$n-C_6H_{13}$	OCHFCF ₃	Н	Н
	Н	OCHFCF ₃	F	Н
	CH₃	OCHFCF ₃	F	Н
35	C₂H₅	OCHFCF ₃	F	Н
	n-C ₃ H ₇	OCHFCF ₃	F	Н

	R	X	L ¹	L ²
	n-C₄H ₉	OCHFCF₃	F	Н
	n-C₅H ₁₁	OCHFCF ₃	F	Н
	n-C ₆ H ₁₃	OCHFCF ₃	F	Н
5	Н	OCHFCF ₃	F	F
	CH₃	OCHFCF ₃	F	F
	C₂H₅	OCHFCF ₃	F	F
	n-C ₃ H ₇	OCHFCF ₃	F	F
	n-C₄H ₉	OCHFCF ₃	F	F
10	n-C₅H₁₁	OCHFCF ₃	F	F
	n-C ₆ H ₁₃	OCHFCF ₃	F	F
	Н	OCF ₂ CHFCF ₃	Н	Н
	CH₃	OCF ₂ CHFCF ₃	Н	Н
	C ₂ H ₅	OCF ₂ CHFCF ₃	Н	Н
15	n-C₃H ₇	OCF ₂ CHFCF ₃	Н	Н
	n-C₄H ₉	OCF ₂ CHFCF ₃	Н	Н
	n-C₅H₁₁	OCF ₂ CHFCF ₃	Н	Н
	n-C ₆ H ₁₃	OCF ₂ CHFCF ₃	Н	Н
	Н	OCF ₂ CHFCF ₃	F	Н
20	CH₃	OCF ₂ CHFCF ₃	F	Н
	C ₂ H ₅	OCF ₂ CHFCF ₃	F	Н
	n-C ₃ H ₇	OCF ₂ CHFCF ₃	F	Н
	n-C₄H ₉	OCF ₂ CHFCF ₃	F	Н
	n-C ₅ H ₁₁	OCF ₂ CHFCF ₃	F	Н
25	n-C ₆ H ₁₃	OCF ₂ CHFCF ₃	F	Н
	Н	OCF ₂ CHFCF ₃	F	F
	CH₃	OCF ₂ CHFCF ₃	F	F
	C₂H₅	OCF ₂ CHFCF ₃	F	F
	n-C₃H ₇	OCF ₂ CHFCF ₃	F	F
30	n-C₄H ₉	OCF ₂ CHFCF ₃	F	F
	n-C ₅ H ₁₁	OCF ₂ CHFCF ₃	F	F
	n-C ₆ H ₁₃	OCF ₂ CHFCF ₃	F	F
	Н	NCS	Н	Н
	CH₃	NCS	Н	Н
35	C₂H₅	NCS	Н	Н
	n-C ₃ H ₇	NCS	Н	Н

	R	X	L¹	L ²
	n-C₄H ₉	NCS	Н	Н
	n-C₅H ₁₁	NCS	Н	Н
	n-C ₆ H ₁₃	NCS	Н	Н
5	Н	NCS	F	Н
	CH₃	NCS	F	Н
	C ₂ H ₅	NCS	F	Н
	n-C₃H ₇	NCS	F	Н
	n-C₄H ₉	NCS	F	Н
10	n-C₅H₁₁	NCS	F	Н
	n-C ₆ H ₁₃	NCS	F	Н
	Н	NCS	F	F
	CH₃	NCS	F	F
	C₂H₅	NCS	F	F
15	$n-C_3H_7$	NCS	F	F
	n-C₄H ₉	NCS	F	F
	n-C₅H₁₁	NCS	F	F
	n-C ₆ H ₁₃	NCS	F	F
	Н	C_2F_5	Н	Н
20	CH₃	C_2F_5	Н	Н
	C ₂ H ₅	C_2F_5	Н	Н
	n-C ₃ H ₇	C_2F_5	Н	Н
	n-C₄H ₉	C ₂ F ₅	Н	Н
	n-C₅H ₁₁	C₂F₅	Н	Н
25	$n-C_6H_{13}$	C₂F₅	Н	Н
	Н	C_2F_5	F	Н
	CH₃	C_2F_5	F	Н
	C_2H_5	C_2F_5	F	Н
00	n-C ₃ H ₇	C ₂ F ₅	F	Н
30	n-C₄H ₉	C ₂ F ₅	F	Н
	n-C₅H ₁₁	C_2F_5	F	Н
	$n-C_6H_{13}$	C_2F_5	F	Н
	Н	C ₂ F ₅	F	F
0.5	CH₃	C_2F_5	F	F
35	C₂H₅	C_2F_5	F	F
	n-C₃H ₇	C_2F_5	F	F

	R	x	L ¹	L ²
	n-C ₄ H ₉	C ₂ F ₅	F	F
	n-C₅H₁₁	C ₂ F ₅	F	F
	n-C ₆ H ₁₃	C ₂ F ₅	F	F
5	Н	C ₃ H ₇	Н	Н
	CH₃	C ₃ H ₇	Н	Н
	C₂H₅	C ₃ H ₇	Н	Н
	n-C ₃ H ₇	C ₃ H ₇	Н	Н
	n-C₄H ₉	C_3H_7	Η .	Н
10	n-C₅H₁₁	C_3H_7	Н	Н
	n-C ₆ H ₁₃	C_3H_7	Н	Н
	Н	C ₃ H ₇	F	Н
	CH₃	C_3H_7	F	Н
	C_2H_5	C_3H_7	F	Н
15	n-C ₃ H ₇	C_3H_7	F	Н
	n-C₄H ₉	C ₃ H ₇	F	Н
	n-C ₅ H ₁₁	C_3H_7	F	Н
	n-C ₆ H ₁₃	C_3H_7	F	Н
	H	C_3H_7	F	F
20	CH₃	C_3H_7	F	F
	C_2H_5	C₃H ₇	F	F
	n-C ₃ H ₇	C₃H ₇	F	F
	n-C₄H ₉	C₃H ₇	F	F
	n-C₅H ₁₁	C₃H ₇	F	F
25	n-C ₆ H ₁₃	C_3H_7	F	F
	Н	SF ₅	Н	Н
	CH₃	SF₅	Н	Н
	C₂H₅	SF₅	Н	Н
00	n-C₃H ₇	SF ₅	Н	Н
30	n-C₄H ₉	SF ₅	Н	Н
	n-C₅H ₁₁	SF ₅	Н	Н
	n-C ₆ H ₁₃	SF ₅	Н	Н
	Н	SF ₅	F	Н
0.5	CH ₃	SF ₅	F	Н
35	C ₂ H ₅	SF ₅	F	Н
	n-C ₃ H ₇	SF₅	F	Н

	R	X	L ¹	L ²
	n-C₄H ₉	SF ₅	F	Н
	n-C₅H₁₁	SF₅	F	Н
	n-C ₆ H ₁₃	SF ₅	F	Н
5	Н	SF ₅	F	F
	CH₃	SF ₅	F	F
	C₂H₅	SF₅	F	F
	n-C₃H ₇	SF ₅	F	F
	n-C₄H ₉	SF₅	F	F
10	n-C ₅ H ₁₁	SF ₅	F	F
	n-C ₆ H ₁₃	SF ₅	F	F
	Н	CN	Н	Н
	CH₃	CN	Н	Н
	C ₂ H ₅	CN	Н	Н
15	n-C ₃ H ₇	CN	Н	Н .
	n-C₄H ₉	CN	Н	Н
	n-C ₅ H ₁₁	CN .	Н	Н
	n-C ₆ H ₁₃	CN	Н	Н
	Н	CN	F	Н
20	CH₃	CN	F	Н
	C_2H_5	CN	F	Н
	$n-C_3H_7$	CN	F	Н
	n-C₄H ₉	CN	F	Н
	n-C ₅ H ₁₁	CN	F	Н
25	n-C ₆ H ₁₃	CN	F	Н
	Н	CN	F	F
	CH₃	CN	F	F
	C₂H₅	CN	F	F
	n-C ₃ H ₇	CN	F	F
30	n-C₄H ₉	CN	F	F
	n-C ₅ H ₁₁	CN	F	F
	$n-C_6H_{13}$	CN	F	F

Mixture examples

|--|

ACQU-3-F

5	CCH-5CF ₃	3.00%	Clearing point [°C]:	+80.0
	CCP-1F.F.F	3.00%	∆n [589 nm, 20°C]:	+0.0660
	CCP-2F.F.F	8.00%	Δε [kHz, 20°C]:	+10.4
	CCP-3F.F.F	8.00%	d · ∆n [20°C, μm]:	0.50
	CCP-5F.F.F	5.00%	Twist [°]:	90
10	CCP-20CF ₃ .F	8.00%	V ₁₀ [V]:	1.31
	CCP-50CF ₃ .F	8.00%		
	CCOC-3-3	2.00%		
	CCOC-4-3	2.00%		
	CCQU-2-F	10.00%		
15	CCQU-3-F	12.00%		
	CCQU-5-F	8.00%		
	ACQU-3-F	15.00%		
	CCH-301	3.00%		
	CCH-501	5.00%		
20				
	Example M2			
	CCH-501	7.00%	Clearing point [°C]:	+88.5
	CCH-5CF ₃	7.00%	∆n [589 nm, 20°C]:	+0.0657
25	CCP-2F.F.F	4.00%	Δε [kHz, 20°C]:	+9.9
	CCP-3F.F.F	7.00%	d - ∆n [20°C, µm]:	0.50
	CCP-5F.F.F	5.00%	Twist [°]:	90
	CCP-30CF ₃ .F	8.00%	V ₁₀ [V]:	1.45
	CCP-50CF ₃ .F	8.00%		
30	CCOC-3-3	3.00%		
	CCOC-3-5	2.00%		
	CCOC-4-3	4.00%		
	CCQU-2-F	10.00%		
	CCQU-3-F	12.00%		
35	CCQU-5-F	8.00%		

15.00%

	Example M3			
	CCH-301	7.00%	Clearing point [°C]:	+81.0
	CCH-501	10.00%	∆n [589 nm, 20°C]:	+0.0608
5	OCH-5CF ₃	2.00%	$\Delta \epsilon$ [kHz, 20°C]:	+8.4
	CCP-2F.F.F	9.00%	d · ∆n [20°C, μm]:	0.50
	CCP-3F.F.F	4.00%	Twist [°]:	90
	CCP-5F.F.F	4.00%	V ₁₀ [V]:	1.49
	CCP-30CF ₃ .F	2.00%		
10	CCP-50CF ₃ .F	4.00%		
	CCOC-3-3	3.00%		
	CCOC-3-5	2.00%		
	CCOC-4-3	4.00%		
	ACQU-3-F	15.00%		
15	CCQU-2-F	10.00%		
	CCQU-3-F	12.00%		
	CCQU-5-F	8.00%		
	CCH-35	4.00%		
20	Example M4			
	CCP-1F.F.F	4.00%	Clearing point [°C]:	+79.0
	CCP-2F.F.F	10.00%	∆n [589 nm, 20°C]:	+0.0808
	CCP-3F.F.F	9.00%	Δε [kHz, 20°C]:	+15.5
25	CCP-5F.F.F	5.00%	d · ∆n [20°C, µm]:	0.50
	CCP-30CF ₃ .F	5.00%	Twist [°]:	90
	CCP-50CF ₃ .F	7.00%	γ₁ [20°C, mPa⋅s]:	150
	PUQU-2-F	5.00%	V ₁₀ [V]:	0.98
	PUQU-3-F	5.00%		
30	CCQU-2-F	11.00%		
	CCQU-3-F	12.00%		
	CCQU-5-F	8.00%		
	CCGU-3-F	4.00%		
	ACQU-3-F	15.00%		
35				

	Example M5			
	BCH-3F.F	10.80%	Clearing point [°C]:	+89.0
	BCH-5F.F	9.00%	∆n [589 nm, 20°C]:	+0.0930
5	ECCP-30CF ₂	4.50%	Δε [kHz, 20°C]:	+6.2
	ECCP-50CF ₃	4.50%		
	CBC-33F	1.80%		
	CBC-53F	1.80%		
	CBC-55F	1.80%		
10	PCH-6F	7.20%		
	PCH-7F	5.40%		
	CCP-20CF ₃	7.20%		
	CCP-30CF ₃	10.80%		
	CCP-40CF ₃	6.30%		
15	CCP-50CF ₃	9.90%		
	PCH-5F	9.00%		
	ACQU-3-F	10.00%		
	Example M6			
20			•	
	CCH-35	3.00%	Clearing point [°C]:	+81.0
	CC-3-V1	4.00%	∆n [589 nm, 20°C]:	+0.0912
	CCP-1F.F.F	10.00%	d · ∆n [20°C, μm]:	0.50
	CCP-2F.F.F	9.00%	Twist [°]:	90
25	CCP-3F.F.F	9.00%	γ₁ [20°C, mPa⋅s]:	129
	CCP-20CF ₃ .F	6.00%	V ₁₀ [V]:	1.30
	CCG-V-F	9.00%		
	CCP-20CF ₃	8.00%		
	CCP-30CF ₃	8.00%		
30	CCP-40CF ₃	6.00%		
	CCP-50CF ₃	7.00%		
	PUQU-2-F	5.00%		
	PUQU-3-F	7.00%		
	APUQU-2-F	4.50%		
35	CGUQU-3-F	3.50%	•	
	CBC-33	1.00%		

	Example M7			
	CCD 25 5 5	11.00%	Clearing point [°C]:	+80.0
	CCP-2F.F.F	7.00%	Δn [589 nm, 20°C]:	+0.1034
E	CCP-20CF₃			0.50
5	CCP-30CF₃	8.00%	d · Δn [20°C, μm]:	90
	CCP-40CF₃	5.00%	Twist [°]:	1.22
	PGU-2-F	8.00%	V ₁₀ [V]:	1.22
	PGU-3-F	7.00%		
40	CC-3-V1	10.00%		
10	CCH-35	3.00%		
	CCP-V-1	5.00%		
	CCP-20CF ₃ .F	8.00%		
	CCP-30CF ₃ .F	11.00%		
	PUQU-2-F	4.00%		
15	PUQU-3-F	6.00%		
	ACQU-3-F	7.00%		
	Example M8			
20	CCP-1F.F.F	6.00%	$S \rightarrow N [^{\circ}C]$:	-40.0
	CCP-2F.F.F	10.00%	Clearing point [°C]:	+80.0
	CCP-20CF₃	8.00%	∆n [589 nm, 20°C]:	+0.1029
	CCP-30CF ₃	8.00%	d · ∆n [20°C, µm]:	0.50
	CCP-40CF₃	6.00%	Twist [°]:	90
25	CCP-50CF₃	8.00%	V ₁₀ [V]:	1.24
	PGU-2-F	8.00%	- "	
	PGU-3-F	7.00%		
	CC-3-V1	8.00%		
	CCH-35	5.00%		
30	CCP-V-1	5.00%		
	CCP-30CF ₃ .F	3.00%		
	PUQU-2-F	4.00%		
	PUQU-3-F	6.00%		
	ACQU-3-F	8.00%		
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	Example M9			
	CC-3-V1	5.00%	S → N [°C]:	-30.0
	CCP-1F.F.F	5.00%	Clearing point [°C]:	+85.5
5	CCP-2F.F.F	8.00%	∆n [589 nm, 20°C]:	+0.0931
	CCP-20CF ₃ .F	8.00%	Δε [kHz, 20°C]:	12.1
	CCP-20CF ₃	5.00%	γ₁ [20°C, mPa⋅s]:	135
	CCP-30CF ₃	8.00%	d · ∆n [20°C, µm]:	0.50
	CCP-40CF ₃	6.00%	Twist [°]:	90
10	CCP-50CF ₃	8.00%	V ₁₀ [V]:	1.23
	PUQU-2-F	5.00%		
	PUQU-3-F	7.00%		
	PGU-2-F	5.00%		
	CCP-V-1	10.00%		
15	ACQU-3-F	12.00%		
	ACQU-4-F	8.00%		
	Example M10			
20	CC-3-V1	6.00%	S → N [°C]:	-40.0
	CCP-1F.F.F	6.00%	Clearing point [°C]:	+83.5
	CCP-2F.F.F	7.00%	∆n [589 nm, 20°C]:	+0.0917
	CCP-20CF ₃ .F	10.00%	Δε [kHz, 20°C]:	11.7
	CCP-20CF ₃	8.00%	γ₁ [20°C, mPa⋅s]:	125
25	CCP-30CF ₃	8.00%	d · Δn [20°C, μm]:	0.50
	CCP-40CF ₃	6.00%	Twist [°]:	90
	CCP-50CF ₃	4.00%	V ₁₀ [V]:	1.25
	PUQU-2-F	5.00%		
	PUQU-3-F	8.00%		
30	PGU-2-F	4.00%		
	CCP-V-1	10.00%		
	ACQU-3-F	10.00%		
	ACQU-4-F	8.00%		

Example M11

	CCH-35	3.00%	Clearing point [°C]:	+81
	CC-3-V1	4.00%	∆n [589 nm, 20°C]:	+0.0912
5	CCP-1F.F.F	10.00%	γ₁ [20°C, mPa⋅s]:	129
	CCP-2F.F.F	9.00%	V ₁₀ [V]:	1.30
	CCP-3F.F.F	9.00%		
	CCP-20CF ₃ .F	6.00%		
	CCG-V-F	9.00%		
10	CCP-20CF ₃	8.00%		
	CCP-30CF ₃	8.00%		
	CCP-40CF ₃	6.00%		
	CCP-50CF ₃	7.00%		
	PUQU-2-F	5.00%		
15	PUQU-3-F	7.00%		
	APUQU-2-F	4.50%		
	CGUQU-3-F	3.50%		
	CBC-33	1.00%		

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Patent Claims

1. Liquid-crystalline compounds of the formula I

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$$R^{1}-(A^{1}-Z^{1})_{a}$$
 $(Z^{2}-A^{2})_{b}$ $-CF_{2}O-(A^{3}-Z^{3})_{c}$ $-A^{4}-R^{2}$ I

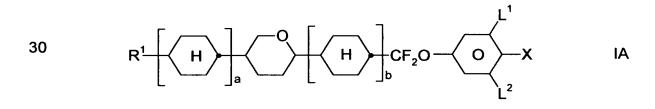
in which

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R¹ and R² each, independently of one another, denote H, a halogenated or unsubstituted alkyl or alkoxy radical having 1 to 15 C atoms, where, in addition, one or more CH₂ groups in these radicals may each, independently of one another, be replaced by -C≡C-, -CH=CH-, -O-, -CO-O- or -O-CO- in such a way that O atoms are not linked directly to one another,

20 $Z^{1}, Z^{2} \text{ and } Z^{3} \qquad \text{each, independently of one another, denote -CO-O-,} \\ -O-CO-, -CF_{2}O-, -OCF_{2}-, -CH_{2}O-, -OCH_{2}-, -CH_{2}CH_{2}-, \\ -(CH_{2})_{4}-, -C_{2}F_{4}-, -CH_{2}CF_{2}-, -CF_{2}CH_{2}-, -CF=CF-, \\ -CH=CH-, -C\equiv C- \text{ or a single bond, and}$

a, b and c each, independently of one another, denote 0, 1 or 2, where $a + b + c \le 2$.

2. Liquid-crystalline compounds of the formula IA



in which

 R^1 , a, b, c and the meanings indicated in Claim 1, where a + b = 1 or 2,

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L¹ and L² each, independently of one another, denote H or F, and

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X denotes F, Cl, CN, or an alkyl, alkenyl, alkoxy or alkenyloxy radical, each having up to 8 C atoms, which is fluorinated by one or more halogen atoms.

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- 3. Liquid-crystalline compounds according to Claim 1 or 2, characterised in that a = 1 and b = 0.
- 4. Liquid-crystalline compounds according to Claim 2, characterised in that L¹ denotes fluorine and L² denotes fluorine or hydrogen.
- 5. Liquid-crystalline compounds according to Claim 2, characterised in that L¹ and L² denote fluorine.
 - 6. Liquid-crystalline compounds of the formulae I1 to I27

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$$R^1 \longrightarrow CF_2O \longrightarrow C$$

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$$R^1$$
 O H CF_2O O X $I2$

$$R^{1}$$
 O H $CF_{2}O$ O F $I3$

$$R^{1} \longrightarrow CH_{2}CH_{2} \longrightarrow H \longrightarrow CF_{2}O \longrightarrow X \qquad 14$$

$$R^{1} \longrightarrow CH_{2}CH_{2} \longrightarrow H \longrightarrow CF_{2}O \longrightarrow X \qquad 15$$

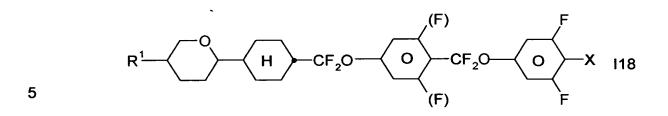
$$R^{1} \longrightarrow CH_{2}CH_{2} \longrightarrow H \longrightarrow CF_{2}O \longrightarrow X \qquad 16$$

$$R^{1} \longrightarrow CH_{2}CH_{2} \longrightarrow H \longrightarrow CF_{2}O \longrightarrow X \qquad 16$$

$$R^{1} \longrightarrow H \longrightarrow CF_{2}O \longrightarrow H \longrightarrow CF_{2}O \longrightarrow X \qquad 17$$

$$R^{1} \longrightarrow H \longrightarrow CF_{2}O \longrightarrow H \longrightarrow CF_{2}O \longrightarrow X \qquad 19$$

$$R^{1} \longrightarrow H \longrightarrow CF_{2}O \longrightarrow G \longrightarrow X \qquad 19$$



$$R^1$$
 H CF_2O O X $I19$

$$R^1$$
 H CF_2O O X $I20$

$$R^1$$
 H CF_2O O X $I21$

$$R^1$$
 \longrightarrow H \longrightarrow CF_2O \longrightarrow X $I22$

$$R^1$$
 O H CF_2O O X $I23$

$$R^1$$
 \longrightarrow H \longrightarrow CF_2O \longrightarrow X \longrightarrow $I24$

10

$$R^1$$
 O O CF_2O O X $I25$

$$R^1$$
 O O CF_2O O X $I26$

$$R^{1} \longrightarrow O \longrightarrow O \longrightarrow CF_{2}O \longrightarrow CF_{2}O \longrightarrow X$$
15

in which R¹ and X have the meanings indicated in Claim 2.

- 7. Liquid-crystalline medium comprising at least two mesogenic compounds, characterised in that it comprises at least one compound of the formula I according to Claim 1.
- 8. Liquid-crystalline medium according to Claim 7, characterised in that it comprises one or more compounds selected from the group consisting of the general formulae II to IX

$$R^{0} \stackrel{\longrightarrow}{\longleftarrow} H \stackrel{\nearrow}{\longrightarrow} Z^{0} \stackrel{\longrightarrow}{\bigcirc} X^{0} \qquad IV$$

$$10 \qquad R^{0} \stackrel{\longrightarrow}{\longleftarrow} H \stackrel{\longrightarrow}{\longrightarrow} Z^{0} \stackrel{\longrightarrow}{\longrightarrow} X^{0} \qquad V$$

$$15 \qquad R^{0} \stackrel{\longrightarrow}{\longleftarrow} H \stackrel{\longrightarrow}{\longrightarrow} C_{2}H_{4} \stackrel{\longrightarrow}{\longrightarrow} X^{0} \qquad VI$$

$$20 \qquad R^{0} \stackrel{\longrightarrow}{\longleftarrow} H \stackrel{\longrightarrow}{\longrightarrow} Z^{0} \stackrel{\longrightarrow}{\longrightarrow} X^{0} \qquad VII$$

$$25 \qquad R^{0} \stackrel{\longrightarrow}{\longleftarrow} H \stackrel{\longrightarrow}{\longrightarrow} Q \stackrel{\longrightarrow}{\longrightarrow} X^{0} \qquad VIII$$

$$30 \qquad R^{0} \stackrel{\longrightarrow}{\longrightarrow} H \stackrel{\longrightarrow}{\longrightarrow} Q \stackrel{\longrightarrow}{\longrightarrow} X^{0} \qquad IX$$

35 in which

	Rº	denotes n-alkyl, oxaalkyl, fluoroalkyl, alkenyloxy or alkenyl, each having up to 9 C atoms,
5	Χo	denotes F, Cl, halogenated alkyl, halogenated alkenyl, halogenated alkenyloxy or halogenated alkoxy having up to 7 C atoms,
10	Z ⁰	denotes -CH=CH-, -C ₂ H ₄ -, -(CH ₂) ₄ -, -C ₂ F ₄ -, -CH ₂ O-, -OCH ₂ -, -CF=CF-, -CF ₂ O-, -OCF ₂ - or -COO-,
10	Y¹,Y², Y³ and Y⁴	each, independently of one another, denote H or F, and
45	r	denotes 0 or 1.
15	9 Use of	the liquid-crystalline medium according to Claim 7 or 8 for

- Use of the liquid-crystalline medium according to Claim 7 or 8 for electro-optical purposes.
- 10. Electro-optical liquid-crystal display containing a liquid-crystalline medium according to Claim 7 or 8.

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Abstract

The invention relates to liquid-crystalline compounds of the formula I

5
$$R^{1}-(A^{1}-Z^{1})_{a}$$
 $(Z^{2}-A^{2})_{b}$ $-CF_{2}O-(A^{3}-Z^{3})_{c}$ $-A^{4}-R^{2}$

in which

R¹, R², A¹, A², A³, A⁴, Z¹, Z², Z³, a, b and c have the meanings indicated in Claim 1, and to liquid-crystalline media comprising at least one compound of the formula I and to electro-optical displays containing a liquid-crystalline medium of this type.

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